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THE TWO TYPES OF X-RAY REFLECTION IN CRYSTALS*

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1. Introduction

One of the most remarkable and fruitful discoveries in modern science was made when Max von Laue applied the principles of the wave-theory to find the effect of passage of a pencil of X-rays through a crystalline plate and arrived at conclusions which were strikingly confirmed by experiment. When the pencil after traversing the crystal is received on a photographic plate, we find recorded on the plate, as predicted by Laue, numerous spots in geometric array, their positions being closely related to the internal atomic architecture of the crystal and the direction of passage of the incident X-rays. The location of the spots in the Laue pattern is determined by the consideration that the secondary radiations from the atoms in the crystal co-operate in the directions indicated by the spots by reason of an agreement in phase, such agreement being itself a consequence of the arrangement of the atoms in a regular space-lattice. The Laue conditions which express this situation are mathematically equivalent to the Bragg formula; the latter follows very simply from the consideration that the crystal is a regularly stratified medium and should, therefore, selectively reflect the radiations falling on its strata at an angle of incidence appropriate to their spacing and to the wave-length of the X-rays in accordance with a general principle familiar to students of optics.

Laue's discovery was a vindication of the wave-theory and was naturally regarded as finally settling the issue, then being keenly debated, whether X-rays were corpuscles or waves, in favour of the latter hypothesis. Actually, however, the position is not quite as simple as this. As we know at the present time, there is an essential duality in the behaviour of the fundamental physical entities. They have a wave-aspect as well as a particle aspect, and these two characters are complementary and not contradictory.

* The new type of X-ray reflection forming the subject of this paper was first described and an explanation of it on the basis of the quantum theory given in a series of papers published earlier this year by Raman and Nilakantan in these Proceedings and elsewhere. The present report is intended to be a self-contained theoretical exposition of the subject and incorporates the ideas already expounded in the papers by Raman and Nilakantan, as also the fuller mathematical treatment by Raman and Nath published in these Proceedings for July 1940. Recent experiments by Nilakantan with diamond completely establish the quantum theoretical explanation of the phenomenon.

To get a complete picture of the observable phenomena, therefore, we can ignore neither one aspect nor the other. It is thus necessary to bear in mind the particle aspect as well as the wave-aspect of the Laue phenomena, and indeed, when we approach the subject from this point of view, the possibility of there being two distinct kinds of X-ray reflection becomes apparent. From the particle point of view, the X-ray reflections of the Laue type are *elastic* collisions of the photon with the crystal lattice, while from the wave-point of view, they arise from the fact that the crystal has a static periodicity of structure. This suggests that a second type of X-ray reflection in crystals should be possible, that from the particle stand-point is an *inelastic* collision in which the photon gives up a part of its energy during the encounter and excites the vibrations of the crystal lattice, while from the wave-stand-point, the reflection is due to the *dynamic stratifications of density* arising from such vibrations of the lattice. From either point of view, a change of frequency is seen to be a necessary feature of the second type of X-ray reflection; we may, therefore, refer to it as the quantum or modified reflection to distinguish it from the classical or unmodified reflections.

2. *Theory of Modified Reflection*

We may now proceed to consider a little more closely the mechanism of the modified X-ray reflection and its relation to the structure of the crystal. The classical or unmodified X-ray reflections arise from the fact that the electron density in the crystal is a periodic function of the co-ordinates in three dimensions. The intensity of the reflection by any particular set of crystal planes is determined by a quantity known as its structure amplitude which specifies the variation of the mean electron density over a plane when such plane is moved normally to itself through the crystal. The positions occupied by the atoms in the unit cell of the lattice are the most important factor in determining the structure amplitudes, though other factors such as the number of electrons and the distribution of electron density in each atom also enter into it.

With scarcely an exception, the actual crystals with which we are concerned contain more than one atom per unit cell, indeed usually several atoms of the same or of different kind. These atoms are held together in their places as the result of forces acting between each atom and its neighbours. Each individual atom is capable of vibrating about its position of equilibrium, but in view of the existence of the interatomic forces, it is more appropriate to consider the crystal lattice as a whole and to fix our attention on some one or another of its possible modes of vibration. These modes fall into two divisions, namely, the vibrations of the acoustic type and

those of the optical type. The vibrations of the acoustic class lie for the greater part in the lower ranges of frequency, while the optical vibrations have frequencies falling in the infra-red region of the spectrum. The character of the movements involved in these two classes differs essentially. The acoustic vibrations consist chiefly of translatory movements of the unit cells of the lattice relative to each other, while in the vibrations of the optical class the atoms within each unit cell oscillate relatively to each other about their common centre of gravity. The interatomic displacements within the unit cells for the acoustic vibrations and the translations of the unit cells for the optical vibrations are in each case of relatively minor importance.

We may now fix our attention on the optical vibrations of the crystal lattice and consider their effect on the structure amplitudes responsible for the X-ray reflections. In the first instance, we may make the simplifying assumption that the oscillation in all the unit cells is of the same frequency, amplitude and phase. It is evident that with this restriction, the atomic vibrations do not affect the uniformity of the crystal structure; the spacing and orientations of the crystal planes remain completely unaltered. The structure amplitudes of the crystal, however, alter periodically with time to an extent depending on the magnitudes and directions of the atomic displacements of which only the components normal to the spacing under consideration are effective. It is evident that the electronic density in the crystal would in these circumstances exhibit two different kinds of space variation, a static structure amplitude which is not a function of time, and a dynamic structure amplitude which varies with time and has the same frequency as the optical vibration of the crystal lattice. If the vibration of the lattice is sufficiently intense, the existence of a dynamic structure amplitude should evidently result in an alteration of the static structure amplitude, in most cases making it smaller than what it would be in the absence of such vibration.

From optical theory, it is evident that a dynamic structure amplitude would result in sharply defined monochromatic reflections in the same way as a static structure amplitude, except that the reflections would now occur with a change of frequency. Since under the assumptions made, the dynamic structure amplitudes do not differ from the static ones in respect of their spacings and orientations, the geometric conditions necessary for the observation of the static and dynamic reflections would also be identical, in other words, these reflections would either appear or not appear together in the same circumstances. If, for instance, the incident X-radiation be monochromatic, neither the modified nor the unmodified reflection would be observable unless the Bragg condition is satisfied.

3. *Geometric Law of Modified Reflection*

We may now remove the restrictive assumption made that the atomic oscillations occur in identically the same phase in all the unit cells comprising the crystal. The oscillation will be assumed to have the same frequency and amplitude everywhere, but its phase will be regarded as variable from cell to cell. While this variation of phase would not affect the *static structure amplitudes* giving the unmodified reflections, it would profoundly influence the *dynamic structure amplitudes* and the effects produced by them. This is very readily seen from the accompanying diagram (Fig. 1), in

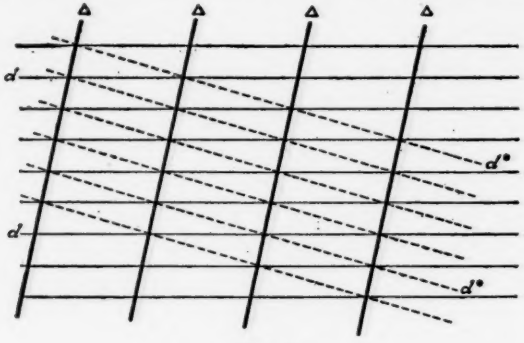

FIG. 1

which the thin lines represent a set of crystal planes and therefore also the planes among which the time-variations of electron density would be the same if the phase of the atomic vibrations were everywhere identical. The heavy lines crossing these at an angle represent the planes along which the phase of the atomic vibrations is constant. It is then evident that the dynamic stratifications of electron density would be along the diagonal planes cutting through the crystal spacings and the phase wave-fronts of the atomic vibration. These diagonal planes are indicated by the dotted lines in the figure, and their spacing and orientation are given by the vectorial formula:

$$\frac{\vec{1}}{d^*} = \frac{\vec{1}}{d} + \frac{\vec{1}}{\Delta} \qquad (1)$$

Here d^* is the spacing of the dynamic stratifications of electron density, d is the static crystal spacing, and Δ the spacing of the phase-waves of the atomic vibration in the crystal lattice. Equation (1) shows that in the limiting case when Δ is infinite, d^* becomes identical with d both in magnitude and direction. The classical and quantum reflections then coincide as already remarked.

So far as the optics of the cases is concerned, the classical and quantum reflections are on a similar footing. For the former to occur, the Bragg condition, namely,

$$2\,d \sin \theta = n\,\lambda \tag{2}$$

must be satisfied, while for the quantum reflections it is similarly necessary that

$$2\,d^* \sin \psi = n\lambda \tag{3}$$

θ and ψ being the glancing angles of the incident beam on the static and dynamic stratifications measured in the respective planes of incidence. Denoting by ϑ and ϵ, the angles which the crystal planes make respectively with the phase-waves and with the dynamic stratifications, we have from equation (1) and Fig. 1,

$$d^* \sin \vartheta = d \sin (\vartheta + \epsilon) = \Delta \sin \epsilon \tag{4}$$

Substituting the first of these relations in (3), we obtain,

$$2\,d \sin \psi \sin (\vartheta + \epsilon) = n\lambda \sin \vartheta. \tag{5}$$

From equation (4), we see that if the wave-length Δ is large compared with the crystal spacing d or the dynamic stratification d^*, the angle ϵ would be small compared with ϑ or $(\vartheta + \epsilon)$. Hence, provided ϑ is not nearly equal to 0 or π, we may write (5) in the *approximate* form

$$2\,d \sin \psi = n\,\lambda \tag{6}$$

which, it will be seen, is merely (3) with d written for d^*, that is to say, with the spacing of the dynamic stratifications put equal to that of the crystal planes from which they are derived. *Equation* (6) *is the same as equation* (2) *with* ψ *written for* θ *and is thus the geometric law for quantum reflections analogous to the Bragg law for the classical reflections.* Since the angular separation between the incident beam and the quantum reflection is $2\,\psi$, equation (6) indicates that within the limits of its validity, *the angular separation of the quantum reflection and the incident beam is independent of the setting of the crystal and is equal to the angular separation of the classical reflection from the incident beam at the Bragg setting of the crystal.*

If Δ is infinite, it follows from (4) that $\epsilon = 0$ and the approximate equation (6) becomes identical with the rigorous equation (5). How nearly this continues to be true when ϵ is finite depends on the angle ϑ. If $\vartheta = \pi/2$, $\sin \vartheta = 1$ and differs little from $\sin (\vartheta + \epsilon)$ even when ϵ is as much as $\pm 10°$. *Hence, for the particular case in which the phase wave-fronts are transverse to the crystal planes, the simple formula* (6) *may be regarded as practically the rigorous geometric law of quantum reflection.* If, however, the inclination ϑ of the phase wave-fronts to the crystal planes is much less

than $\pi/2$, it is not permissible to write $\sin\vartheta = \sin(\vartheta + \epsilon)$ except for very small values of ϵ, and hence in such a case, the rigorous formula (5) should be employed. It is evident that the angular separation 2ψ of the quantum reflection from the incident beam would not then be independent of the crystal setting, but would be greater or less than the fixed value given by equation (6) according as ϵ is negative or positive, that is to say, according as the tilt of the dynamic stratifications with respect to the crystal planes is one way or the other.

The static and dynamic reflecting planes are coincident when Δ is infinite and ϵ is therefore zero. The planes of incidence for both reflections are, therefore, identical in this particular case. If this result be true generally, *it would follow that the quantum reflection by any particular crystal spacing appears in the same plane of incidence as the usual Laue reflection.* We may then write $2\psi = (\theta + \phi)$ and $2\epsilon = (\phi - \theta)$, ϕ being the glancing angle of the quantum reflection measured with reference to the crystal planes. Equation (5) then becomes

$$2d \sin\frac{\phi + \theta}{2} \sin\left(\vartheta + \frac{\phi - \theta}{2}\right) = n\lambda \sin\vartheta \tag{7}$$

while equation (6) takes the form

$$2d \sin\tfrac{1}{2}(\phi + \theta) = n\lambda \tag{8}$$

It is easily seen that the rigorous formula (7) would in every case give values of ϕ closer to θ than the approximate formula (8), the difference being least when $\vartheta = \pi/2$. In general, therefore, when ϑ is less than $\pi/2$, *the quantum reflection is nearer the Laue reflection than the fixed position indicated by the approximate formula*; *it moves in the same direction as the Laue spot, though much more slowly, as the crystal is rotated*; *it coincides with and is overtaken by the Laue spot at the Bragg setting and continues to follow its further movement as the crystal is turned away from that setting.* In the limiting case when $\vartheta = 0$, equation 7 indicates that $\phi = \theta$, in other words, the quantum reflection appears superposed on the Laue spot.

4. *Intensity of Modified Reflection*

The modified reflection is the result of the crystal taking up a quantum of energy $h\nu^*$ and the photon going off with the remainder of the energy $h(\nu - \nu^*)$, ν and ν^* being the frequency of the incident radiation and of the lattice vibrations respectively. The energy $h\nu^*$ being shared by all the lattice cells in the crystal, the amplitude of vibration and the resulting dynamic structure amplitude would be exceedingly small. It might, therefore, seem at first sight that the probability of the process occurring would

be negligible. Actually, however, the small probability of the individual process is set off by the fact that the number of lattice cells N in the crystal is enormously large, and the system therefore possesses N discrete frequencies of vibration ranging around the value ν^*. The fraction $d\,\mathrm{N}/\mathrm{N}$ of this large number which becomes effective in any particular circumstances determines the observed intensity of the quantum reflection. This fraction should clearly be a function of the magnitude and direction of the phase vector $1/\Delta$ which we shall denote for convenience by the symbol δ. We may, therefore, write

$$d\,\mathrm{N}/\mathrm{N} = \frac{1}{4\pi}\,\mathrm{G}\,(\delta, \chi, \vartheta)\,\sin\vartheta\, d\vartheta\, d\chi\, d\delta. \tag{9}$$

In this equation, ϑ is the angle already introduced, namely the inclination of the phase wave-fronts to the crystal strata. χ is the azimuth of a plane normal both to the crystal strata and to the phase wave-fronts, the reference plane for which $\chi = 0$ being the plane of incidence on the crystal strata. $\sin\vartheta d\vartheta d\chi$ is, therefore, the elementary solid angle within which the vector δ lies.

The dependence of the G-function upon the value of δ should evidently be very pronounced. Since the characteristic frequency ν^* corresponds to a zero value of δ, we may expect the possible degrees of freedom to cluster densely around small values of δ and to thin out for large values of δ. In other words, the G-function would have a strongly marked maximum when $\delta = 0$ and diminish rapidly as δ increases. If, therefore we regard the other variables in the function as having fixed values, *e.g.*, $\chi = 0$ and $\vartheta = \pi/2$, the variation of intensity of the quantum reflection would depend solely on the value of δ determined by the angles of incidence and reflection. It would then follow from equation (1) that *the intensity of the quantum reflection would be a maximum at the Bragg setting of the crystal for which* $\phi = \theta$ *and would fall off rapidly as the crystal is moved away from this setting in either direction.*

It will be noticed that we have written the G-function with the angles χ and ϑ appearing explicitly in it, thereby indicating that the number of degrees of freedom lying between given limits of δ depends on the inclination of the wave-fronts to the crystal planes and also on the azimuth of the plane which is normal to both the static and dynamic stratifications of density. Such a dependence is to be expected on dynamical grounds. It is well-known that in a crystal, the relation between wave-length and frequency for vibrations of the *acoustic class* is a function both of the direction of vibration and the direction of propagation, the wave-front splitting up into a surface of three sheets even in a cubic crystal. There would, therefore,

be no justification for assuming that for vibrations of the optical class, the distribution of the degrees of freedom would be independent of either the orientation of the wave-fronts in the crystal, or of the directions of the atomic vibration in them. In our present problem, we are concerned with the modes of vibration in which the displacements of the atoms are predominantly normal to the particular crystal planes under study, since displacements parallel to the planes have no effect on their structure amplitudes. We may, therefore, reasonably anticipate that the G-function should show a strongly marked dependence on the angles ϑ and χ which enter in our problem.

It is evident that if the angles ϑ, χ defining the orientation of the phase-waves are regarded as entirely arbitrary, the optical conditions necessary for a reflection of the X-rays would be insufficient to indicate a unique direction for such reflection for any given setting of the crystal. It is, however, easily shown analytically or geometrically that they suffice to indicate a direction which would correspond to a minimum value of δ and therefore also to a maximum observable intensity of reflection, the values of χ and ϑ corresponding to such direction being 0 and $(\pi/2-\phi)$ respectively. The zero value of χ indicates that the reflection would be in the plane of incidence, while the value $(\pi/2-\phi)$ on substitution for ϑ in (7) yields the formula

$$d \sin(\phi+\theta) = n\lambda \cos\phi \tag{10}$$

which may also be written as

$$d(\sin\theta + \cos\theta \tan\phi) = n\lambda \tag{11}$$

both reducing to the Bragg formula when $\theta = \phi$.

The considerations on which equation (11) *is based would, however, be invalid and the results given by this formula would be contradicted by experiment*, if the angles ϑ and χ appear explicitly in the distribution function $G(\delta, \chi, \vartheta)$ as assumed in our equation (9). For, when this is the case, the maximum of this function would be determined, not solely by the variations of δ, but also by the independent variations of χ and ϑ, and the preferred values of these angles which make the G-function a maximum must, therefore, influence both the intensity of the modified reflection as well as the plane and direction in which it is observed. The value of χ determines the plane of reflection, while that of ϑ notably influences the direction of reflection in that plane. Hence the more precisely these angles can be specified, the more sharply defined would the direction of reflection be. The dependence of the distribution function on the angle variables thus plays an important part in determining all the observable features of the quantum reflection, namely,

the plane and the direction in which it is to be found, its sharpness and its intensity. The preferred value of ϑ is in particular of special importance and may be expected to depend on the substance chosen for investigation and possibly even on the particular set of crystal planes from which the reflections are observed. It may be evaluated by observing the quantum reflections over a sufficiently wide range of settings of the crystal and comparing the experimental results with the general formula (5) or its near equivalent (7).

5. *Effect of Acoustic Vibrations*

We may now briefly discuss the phenomena resulting from the excitation of those crystal vibrations which lie in the acoustic range of frequency. When the number of atoms in the unit cell of the lattice is fairly large, the proportion of the aggregate number of degrees of freedom appearing as acoustic vibrations is small and the effects due to them are of small importance compared with those arising from the optical vibrations. Nevertheless, they deserve some consideration. The distinguishing feature of the acoustic vibrations is that they involve translatory movements of the unit cells, in other words a disordering of the crystal lattice, while the optical vibrations involve such movements to a negligible extent and may, therefore, be excited without distorting the crystal lattice. We have already noticed the latter as the special feature which enables the crystal to give modified or quantum reflections. We shall presently see that no such reflections would result from crystal vibrations of the acoustic class, and that on the contrary these vibrations would give rise only to a diffuse scattering of the X-rays.

A longitudinal sound-wave causes the mean electronic density in a crystal to vary periodically, and if its wave-length is sufficiently large in relation to the spacing of the lattice planes, we may ignore the latter and regard the wave itself as a time-periodic stratification of electronic density. Accordingly, the X-ray photon impinging on the crystal should excite such sound waves by inelastic collision and itself be reflected in the process, provided that the length Δ of the sound-wave, the glancing angle θ on its wave-fronts and the X-ray wave-length λ satisfy the relation

$$2\,\Delta \sin\theta = \lambda. \tag{12}$$

Accordingly, since both Δ and θ are arbitrary, the effect here contemplated would give rise to a diffuse scattering in directions surrounding the incident beam and lying within a cone of semi-vertical angle $2\,\theta$ determined by the limiting value of θ at which the argument fails, namely, when Δ is of the same order of magnitude as the lattice spacings in the crystal.

To find the phenomena in directions lying outside this cone, the procedure to be followed would be formally analogous to that indicated earlier for the optical vibrations, namely, to analyse the structure amplitudes of the crystal into a static part and a dynamic part having the frequency of the acoustic vibration, and to consider the effect of the latter separately. The detailed results would, however, be quite different from those obtained for the optical vibrations. While an infinite wave-length Δ for the optical vibrations corresponds to one or other of the characteristic frequencies at which there is a maximum concentration of the degrees of freedom of the system, we have exactly the opposite situation in the acoustic case, the infinite wave-length then corresponding to zero frequency and a minimum concentration of the degrees of freedom. Hence the arguments which indicate that in the optical case the reflected beam is limited to particular directions in the plane of incidence are wholly inapplicable for the acoustic vibrations.

We conclude that *the acoustic vibrations of the crystal lattice, though they may be excited by an inelastic collision of the photon, give rise to a diffuse scattering without any pronounced directional effects.*

6. *Analogy with Light Scattering*

As is well-known, when monochromatic light traverses a crystal and the light diffused by it is spectroscopically examined, the scattered radiations exhibit diminished and in some cases also enhanced frequencies. The frequency shifts fall into two classes. Some of them are very small and require for their observation the use of a Lummer-Gehrcke plate or a Fabry-Perot etalon; the shifts are found to depend on the direction of observation and evidently arise from the acoustic vibrations of the crystal lattice. The second group of frequency shifts may be observed with an ordinary spectroscope and correspond to those optical vibrations of the crystal lattice which are active in light scattering. In the latter case, no variations with the direction of observation have been reported, though no very careful investigations appear to have been made on this question.

It is recognised that the scattering of light with change of frequency is a quantum effect, though it has a classical analogue which fails to represent the observed facts in essential particulars. There is thus a clear analogy between the modified scattering of light and the quantum reflection of X-rays, both phenomena arising from the inelastic collisions of photons with crystals. The wave-length of the incident radiation is widely different in the two cases, and this is largely responsible for the difference in the character of the resulting effects. Despite the obvious differences, the fundamental similarity in the processes involved and the phenomena observed should

be useful as a guide to research in both fields of investigation. In particular, it is desirable to emphasise that, as in the case of X-rays, the change of frequency observed in light-scattering should be regarded as the co-operative effort of extended domains in the crystal and not the effect of the individual ions or molecules in it.

In the literature of light-scattering, we are familiar with the idea that certain optical modes are active while others are inactive, the distinction being largely determined by the symmetry characters of the vibration. In the X-ray problem, the question whether an optical vibration is 'active' in giving a modified reflection depends on whether it modifies the structure amplitude of the particular crystal spacing under study. It is evident, however, that in the X-ray problem we are dealing with the superposed effect of all the characteristic optical modes, and cannot isolate the effect of any one of them in particular. On the other hand, we can observe the modified reflection from numerous individual crystal planes and the geometric relation of such planes to the various optical modes of vibration of the lattice cells would naturally be different. The X-ray method is also capable of application to crystals with which optical study is difficult or impossible. Hence a study of the phenomena of the modified X-ray reflection may be expected to lead us to a deeper understanding of the problem of crystal physics, and to supplement in important respects the results of spectroscopic studies.

7. *Influence of Temperature*

The analogy with light scattering is particularly useful in considering how the intensity of modified X-ray reflection would be influenced by varying the temperature of the crystal. As is well known, the character of the phenomena observed in light scattering differs essentially in the two cases in which $h\nu^* \gg \mathrm{K\,T}$ and $h\nu^* \ll \mathrm{K\,T}$ respectively. In the first case, the thermal agitation of the system plays an insignificant rôle, and the scattering is due to its transitions from the lowest to higher energy-levels induced by the incident radiation. Hence, the scattering is with diminished frequency only, and its intensity is independent of temperature, being much greater than that indicated by classical considerations for a vibration with energy K T. In the second case in which $h\nu^* \ll \mathrm{K\,T}$, the observed effects are practically describable in terms of the classical theory: the intensity of the scattering increases in proportion to the absolute temperature and appears to an equal extent with diminished and with increased frequencies. In the intermediate cases when $h\nu^*$ and K T are of comparable magnitudes, the scattering with diminished frequency is of greater intensity than that with increased frequency. The ratio of the two tends to approach unity as the

temperature is raised, and the absolute intensities of both types of scattering also become larger. This is because the transition probabilities from a thermally excited state are greater than from the ground state of the system.

We may naturally expect very similar results in the case of modified X-ray reflection, except that as it is not possible to separate the reflections with diminished and increased frequencies, we are only concerned with the result of their summation. As indicated by the theory, the nature of the results would depend on the characteristic optical frequencies of the crystal. At sufficiently low temperatures, the indications of the classical theory should in every case fail completely, and the quantum reflections, instead of vanishing, should continue to be observable. Further, for crystals with high characteristic frequencies, the intensity of reflection should be much greater than that indicated by the classical considerations, and its increase with rise of temperature should also be slower. On the other hand, for crystals with relatively low characteristic frequencies, the increase of intensity with temperature should be very marked. Further, since this increase indicates a larger population of thermally excited states and therefore also a diminution of the static structure amplitudes, *the increase of intensity of the modified X-ray reflections with rise of temperature would be accompanied by a falling off in the intensity of the unmodified reflections.*

It follows from the foregoing remarks that theories of the temperature effect in X-ray diffraction based on classical considerations cannot be expected to be in full accord with the facts either at low or high temperatures. This is indeed evident from the published literature of the subject. In the treatments usually given, however, the classical considerations are modified by taking into account the zero-point energy of the vibrations of the crystal and assuming that these have an optical effect analogous to that of thermal agitation. The static structure amplitudes of the crystal at low temperatures are thereby brought into better accord with the observed facts. It is evident, however, that except in regard to the classical or unmodified reflections, the effects produced by the crystal on the incident radiation depend on the change in the energy-state of the crystal and not upon its initial energy. The zero-point energy is therefore not really relevant to the discussion of such effects.

8. *Summary*

The X-ray reflections of the Laue type are elastic collisions of the photons with the crystal considered as a structure with static space periodicities. The modified or quantum reflections are inelastic collisions in which the photon excites the vibration of the crystal lattice and is itself reflected by

the dynamic stratifications of electron density arising from such vibrations. The quantum reflections obey the Bragg principle with respect to the dynamic spacings, these however, in general, differing from the static spacings, besides being differently oriented, except when the incidence on the static spacings is at the Bragg angle for the given monochromatic radiation, in which case they are identical. The general geometric formula for the quantum reflection is

$$2d \sin \frac{\phi + \theta}{2} \sin \left(\vartheta + \frac{\phi - \theta}{2}\right) = n \lambda \sin \vartheta$$

where θ and ϕ are the glancing angles of incidence and reflection, and ϑ is the inclination of the phase-waves to the crystal spacings. If ϑ does not differ greatly from $\pi/2$, this reduces approximately to the symmetric formula $2d \sin \frac{1}{2}(\theta + \phi) = n\lambda$. All the observable features of the quantum reflection are determined by the properties of the G-function which gives the distribution of the degrees of freedom of optical vibration as determined by the reciprocal of the length of the phase-waves of the optical vibration of the lattice and the angle variables ϑ, χ defining their orientation. The dependence on temperature of the intensity of quantum reflection is very different in the two cases where $h\nu^* \gg \mathrm{KT}$ and $h\nu^* \ll \mathrm{KT}$ where ν^* is the optical frequency of the lattice vibration. The increase of intensity of the modified X-ray reflections with rise of temperature is accompanied by a falling off in the intensity of the unmodified reflections from the same spacings.

THE LOCALISATION OF THE DISCHARGE IN ORDINARY AND CANAL-RAY TUBES

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§ 1. It is known,[1] that the discharge glow near the cathode in the case of both an ordinary and canal ray discharge tube, shows significant changes with increase in the excitation voltage. At low values of the order of a kilovolt, visually, this glow is found to occupy the whole of the cathode surface. As the voltage across the tube is increased, its cross-section decreases rapidly until at voltages of the order of five to six kilovolts, it is strictly confined to the centre-most region of the cathode surface. Its length, on the other hand, shows a proportionate increase. If we use a number of canals instead of one, we observe the same phenomenon ; at higher voltages the positive rays fill only the central canal whereas the others but show feeble emission. It is evident that the intensity of the positive ray beam obtained in a canal ray tube, will be determined to a considerable extent by the phenomenon of localisation. The reason for this localisation under either type of the discharge conditions is not known, but has been generally ascribed to the presence of a space-charge, on the walls of the discharge tube.

The present paper describes a more direct method than the visual, in which the localisation has been quantitatively investigated by observations on the radial distribution of the current on the cathodic surface, by using a sectorial cathode. The method is essentially similar to that used by Yarnold and Holmes[2] for finding the radial distribution of the electrons on the anode surface in the case of the uniform column of the electric discharge. In the present paper, this distribution is studied as a function of the applied voltage and in the latter part as that of the length of the cathode dark space, in the case of different gases.

An interpretation of the radial distribution of the current on the cathodic surface in terms of the corresponding distribution amongst the impacting positive ions is found to be possible by making certain simplifying assumptions. These are finally discussed with reference to the experimental results obtained.

§ 2. The experimental arrangement used in this investigation consists of a discharge tube 3·5 cm. in diameter provided with an aluminium anode fitted in a side tube and a composite cathode consisting of three rings or sectors of moulded aluminium insulated from each other by thin sectors of ebonite. The first sector extends from the centre to 0·4 cm. and has an area of 0·50 cm.^{2} The second lies between 0·5 cm. and 0·95 cm. from the centre with an area of 2·05 cm.^{2} The third covers a region between 1·1 cm. to 1·55 cm. from the centre and an area of 3·74 cm.^{2} The cathode is also provided with a canal of 0·2 cm. in diameter and 0·7 cm. in length ; when required the central canal can be closed with an aluminium rod, when it will function as an ordinary cathode. The three sectors of the cathode are separately earthed through sensitive milliammeters. The H.T. used is obtained from a transformer coupled with a single Kenotron circuit, thus giving a half-wave rectified current. The secondary voltage is measured by means of an electrostatic voltmeter of the Kelvin-Whyte type. Evacuation is obtained by means of a set of mercury diffusion pumps of the Waran type backed by a Cenco-Hyvac oil pump. Liquid air traps are used for preventing the diffusion of mercury vapour into the discharge tube as also for purifying the gases. The gases used are hydrogen, air, nitrogen and oxygen. Nitrogen is obtained from a cylinder and is purified by bubbling through pyrogallol. The purification of hydrogen is performed by passing it over heated magnesium and copper filings. No such arrangement is found to be necessary for oxygen which is obtained by heating pure potassium-permanganate in vacuum. All the gases are dried and purified by passing over a number of suitable drying agents before being allowed to enter into the discharge tube. Special care is taken to avoid heating of the discharge tube, and the electrodes, by interrupting the discharge for a suitable time interval between two successive readings. This precaution is found to be necessary for obtaining reproducible results. Gas-streaming is used for the majority of the experiments. Preliminary experiments with and without streaming are found to give identical results.

§ 3. The variation in the currents received by the three sectors in the case of air and hydrogen, with the voltage is shown in Tables 1, 2. Here M_1, M_2, M_3 represent the currents received by the three sectors starting with the innermost, M being the total current ($M_1 + M_2 + M_3$). From a knowledge of these values it is possible to find the distribution of the current density on the cathodic surface by finding empirical relations to fit the observed values. It is found, that the results can be explained if we assume that the distribution of the current density on the cathode surface is given by

$$i = A\, e^{-h^2 r^2}$$

where h is a constant which varies with the voltage across the discharge tube (or the length of the cathode dark space). The value of i will be a maximum for $r = 0$ and will have the value A. It will be observed therefore, that h determines the distribution of the current density on the cathode surface. Therefore

$$M_1/M = \frac{\int_0^{r_1} e^{-h^2r^2}.\,2\pi r dr}{\int_0^{r_3} e^{-h^2r^2}.\,2\pi r dr}; \qquad M_2/M = \frac{\int_{r_1}^{r_2} e^{-h^2r^2}.\,2\pi r dr}{\int_0^{r_3} e^{-h^2r^2}.\,2\pi r dr}$$

$$M_3/M = \frac{\int_{r_2}^{r_3} e^{-h^2r^2}.\,2\pi r dr}{\int_0^{r_3} e^{-h^2r^2}.\,2\pi r dr}$$

where r_1, r_2, r_3, represent the outer radii of the three sectors respectively. The area covered by the insulation material has been here neglected as an approximation. From the experimental value of M_1/M we can calculate the value of h. This when substituted gives the theoretical values for M_2/M and M_3/M. Tables 1 and 2 show both the experimental and the

TABLE 1. *Canal-Ray Discharge in Hydrogen*

Total current = 1·60 m.a.

Discharge voltage in kV.	h	M_1/M		M_2/M		M_3/M	
		Exp.	Theor.	Exp.	Theor.	Exp.	Theor.
1·20	1·992	0·47	0·47	0·50	0·50	0·03	0·028
1·65	2·361	0·59	0·59	0·37	0·40	0·03	0·007
2·00	2·458	0·62	0·62	0·34	0·38	0·03	0·004
2·45	2·822	0·72	0·72	0·25	0·28	0·03	0·001
2·75	2·945	0·75	0·75	0·22	0·25	0·03	0·000
3·20	3·077	0·78	0·78	0·19	0·19	0·03	0·000
3·50	3·386	0·84	0·84	0·12	0·16	0·03	0·000
3·90	3·386	0·84	0·84	0·12	0·16	0·03	0·000
4·35	3·386	0·84	0·84	0·12	0·16	0·03	0·000
4·90	3·386	0·84	0·84	0·12	0·16	0·03	0·000

TABLE 2. *Canal-Ray Discharge in Air*

Total current = 1·60 m.a.

Discharge voltage in kV.	h	M_1/M		M_2/M		M_3/M	
		Exp.	Theor.	Exp.	Theor.	Exp.	Theor.
1·35	1·527	0·31	0·31	0·62	0·56	0·06	0·13
2·05	1·787	0·40	0·40	0·56	0·57	0·09	0·037
2·65	2·203	0·54	0·54	0·40	0·44	0·03	0·016
3·15	2·361	0·59	0·59	0·37	0·40	0·03	0·007
3·45	2·392	0·60	0·60	0·36	0·39	0·03	0·006
3·95	2·711	0·69	0·69	0·28	0·31	0·03	0·001
4·60	2·869	0·73	0·73	0·23	0·27	0·03	0·001
5·15	3·077	0·78	0·78	0·19	0·22	0·03	0·000
5·70	3·222	0·81	0·81	0·16	0·19	0·03	0·000

theoretical values side by side. It will be observed that they show a sufficiently close agreement.

The actual radial distribution of the current as calculated from a knowledge of the value of h for different voltages in the case of air and hydrogen, are shown in Figs. 1 and 2. The increased localisation with increase in the voltage across the discharge tube is well shown by the curves in the figures. Fig. 3 gives the variation of the current density at a distance of 0·5 cm. from the centre of the cathode with voltage in the case of the gases investigated. The curves in the different figures show that the current density in the centre of the cathode is always considerably greater than that found elsewhere. This observation has been verified later even for low voltages ($< < 1{\cdot}0$ kV.).

§ 4. Certain observations during the course of the above work led to the suspicion that the radial distribution of the current is determined to a greater extent by the length of the cathode dark space than by the operating voltage across the tube. During the second part of the investigation, this therefore is chosen as the variable, the corresponding values of the voltage are also given for comparison. Some of the results in the case of the different gases, for different current strengths under conditions of ordinary and canal-ray discharge are given in Tables 3–10. The current values are now expressed as fractional current per unit area received by each sector. Under

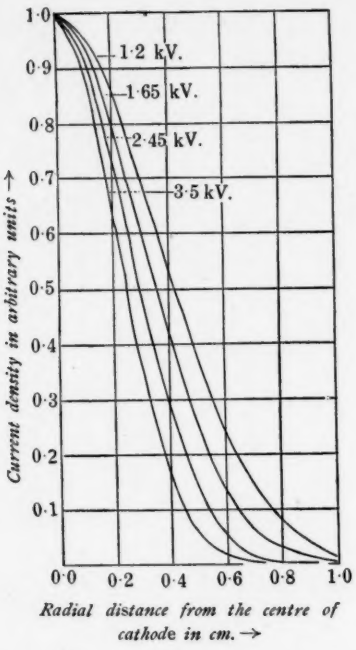

FIG. 1
Canal-Ray Discharge in Hydrogen

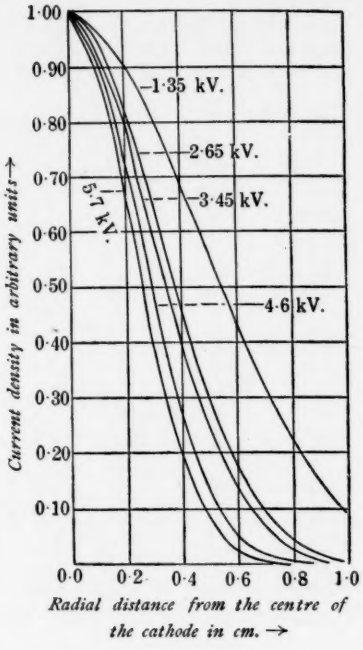

FIG. 2
Canal-Ray Discharge in Air

the conditions of canal-ray discharge the area of the first sector diminishes by an amount 0·03 cm.^{2} on account of the opening of the central canal. On the other hand we have to take into consideration the current received by the inner wall of the canal which has an area of 0·44 cm.^{2} The effective part of this area depends on the canal-ray beam-divergence which is a function of the voltage. It is thought therefore advisable to neglect the uncertain increase in the area and take count only of the decrease on account of the central opening. It is therefore clear that the fractional current densities given in the tables for the conditions of the canal-ray discharge will be considerable higher estimates of the actual values, especially for low voltages where the beam-divergence is most pronounced. This discrepancy will tend to decrease with increasing voltage. This fact should be given proper consideration when comparing the results obtained under conditions of ordinary and canal-ray discharge. Each table gives the mean of at least two sets of observations. The standard deviation is given in the case of some of the observations to give an idea of the reproducibility of the results.

TABLE 3. *Ordinary Discharge in Hydrogen*

Total current = 1·00 m.a.

D.S.L. in cms.	H.T. in kV.	M_1/MA_1	M_2/MA_2	M_3/MA_3
0·2	..	0·42	0·24	0·08
0·4	..	0·32	0·19	0·12
0·5	..	0·21	0·20	0·13
1·0	..	0·21	0·20	0·13
1·5	..	0·32	0·29	0·09
2·0	..	0·42	0·29	0·05
2·5	..	0·64	0·29	0·03
3·0	..	0·95	0·27	0·01
3·5	1·5	1·27	0·20	0·01
4·0	2·5	1·59	0·12	0·01
4·5	3·5	1·80	0·07	0·01
5·0	4·6	1·91	0·05	0·01

TABLE 4. *Ordinary Discharge in Hydrogen*

Total current = 2·00 m.a.

D.S.L. in cms.	H.T. in kV.	M_1/MA_1	M_2/MA_2	M_3/MA_3
0·2	..	0·32	0·24	0·09
0·3	..	0·25	0·21	0·12
0·5	..	0·21	0·15	0·16
0·8	..	0·21	0·15	0·16
1·0	..	0·21	0·17	0·15
1·5	..	0·32	0·24	0·09
2·0	..	0·42	0·29	0·05
2·5	..	0·64	0·29	0·03
3·0	1·3	0·85	0·27	0·01
3·5	2·5	1·21	0·20	0·01
4·0	3·5	1·49	0·14	0·01
4·5	5·0	1·70	0·10	0·00
5·0	5·8	1·91	0·05	0·00
5·5	6·6	1·91	0·05	0·00

TABLE 5. *Ordinary Discharge in Hydrogen*

Total current = 1·60 m.a.

D.S.L. in cms.	H.T. in kV.	M_1/MA_1	M_2/MA_2	M_3/MA_3
0·2	..	0·38	0·24	0·08
0·5	..	0·20	0·15	0·16
1·0	..	0·32	0·20	0·13
1·5	..	0·32	0·24	0·09
2·0	..	0·44	0·30	0·04
2·5	..	0·62	0·30	0·02
3·0	1·2	1·11	0·20	0·01
3·5	2·9	1·19	0·18	0·01
4·0	3·3	1·45	0·12	0·00
4·5	4·6	1·72	0·06	0·00
5·0	5·8	1·72	0·05	0·00
Standard deviation =		0·01	0·003	0·001

TABLE 6. *Canal-Ray Discharge in Hydrogen*

Total current = 1·60 m.a.

D.S.L. in cms.	H.T. in kV.	M_1/MA_1	M_2/MA_2	M_3/MA_3
0·2	..	0·25	0·24	0·10
0·5	..	0·19	0·15	0·16
1·0	..	0·19	0·18	0·14
1·5	..	0·25	0·24	0·10
2·0	..	0·40	0·30	0·05
2·5	..	0·59	0·30	0·02
3·0	0·9	0·72	0·29	0·02
3·5	2·2	0·96	0·24	0·01
4·0	3·5	1·31	0·17	0·01
4·5	4·5	1·59	0·11	0·01
5·0	6·0	1·70	0·06	0·01
Standard deviation =		0·01	0·003	0·001

TABLE 7. *Ordinary Discharge in Air*

Total current = 1·60 m.a.

D.S.L. in cms.	H.T. in kV.	M_1/MA_1	M_2/MA_2	M_3/MA_3
0·1	..	0·24	0·24	0·10
0·3	..	0·20	0·14	0·16
0·5	..	0·18	0·14	0·16
1·0	..	0·18	0·18	0·14
1·5	..	0·24	0·26	0·09
2·0	..	0·38	0·30	0·05
2·5	0·8	0·56	0·31	0·02
3·0	1·9	0·70	0·30	0·01
3·5	2·8	0·91	0·24	0·01
4·0	3·8	1·29	0·16	0·01
4·5	5·2	1·55	0·10	0·00
5·0	6·1	1·73	0·06	0·00
	Standard deviation =	0·02	0·01	0·001

TABLE 8. *Canal-Ray Discharge in Air*

Total current = 1·60 m.a.

D.S.L. in cms.	H.T. in kV.	M_1/MA_1	M_2/MA_2	M_3/MA_3
0·2	..	0·19	0·15	0·02
0·5	..	0·19	0·14	0·16
1·0	..	0·21	0·18	0·14
1·5	..	0·25	0·24	0·10
2·0	..	0·40	0·30	0·05
2·5	0·8	0·53	0·30	0·03
3·0	1·8	0·66	0·30	0·01
3·5	2·8	1·04	0·23	0·01
4·0	3·9	1·36	0·17	0·01
4·5	5·3	1·59	0·10	0·01
5·0	6·4	1·72	0·06	0·01
	Standard deviation =	0·01	0·002	0 001

TABLE 9. *Canal-Ray Discharge in Oxygen*

Total current = 1·60 m.a.

D.S.L. in cms.	H.T. in kV.	M_1/MA_1	M_2/MA_2	M_3/MA_3
0·2	..	0·17	0·26	0·09
0·5	..	0·15	0·12	0·18
1·0	..	0·21	0·17	0·14
1·5	..	0·25	0·24	0·10
2·0	..	0·40	0·28	0·05
2·5	1·4	0·55	0·30	0·03
3·0	2·5	0·72	0·29	0·02
3·5	3·6	1·06	0·22	0·01
4·0	4·7	1·32	0·16	0·01
4·5	6·0	1·49	0·12	0·01
	Standard deviation =	0·01	0·002	0·001

TABLE 10. *Canal-Ray Discharge in Nitrogen*

Total current = 1·60 m.a.

D.S.L. in cms.	H.T. in kV.	M_1/MA_1	M_2/MA_2	M_3/MA_3
0·2	..	0·19	0·13	0·16
0·5	..	0·17	0·15	0·16
1·0	..	0·25	0·18	0·13
1·5	..	0·25	0·24	0·09
2·0	..	0·40	0·29	0·05
2·5	1·5	0·53	0·30	0·03
3·0	2·4	0·74	0·28	0·02
3·5	3·3	1·06	0·22	0·01
4·0	4·5	1·38	0·14	0·01
4·5	5·5	1·61	0·10	0·01
5·0	7·5	1·72	0·06	0·01
	Standard deviation =	0·01	0·001	0·001

§ 5. A reference to these tables shows that the fractional current values tend to become stationary for high values of the D.S.L. (length of the cathode dark space). Thus the fractional current density over the first sector shows, *e.g.*, Table 4, a stationary maximum value of 1·91 and the two others stationary minimum values of 0·05 and 0·00 respectively. These values are not found to alter sensibly by a variation of the total current passing through the discharge tube (*vide* Tables 3, 4 and 5) and therefore represent stationary values of the fractional current densities and not of the current densities in the absolute sense. It is also seen that the fractional current received by the first sector is always considerably greater than that obtained elsewhere under the different conditions of experiment, showing that there is a concentration of current density in the centre under all the conditions considered here. Observations indicate that practically similar remarks hold good for conditions of canal-ray discharge also. We can therefore make use of the empirical relation, to find the actual radial distribution of the current density on the cathode surface. Fig. 4 shows the variation of the current density on the

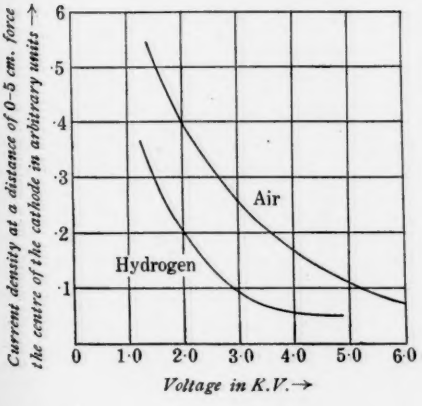

FIG. 3

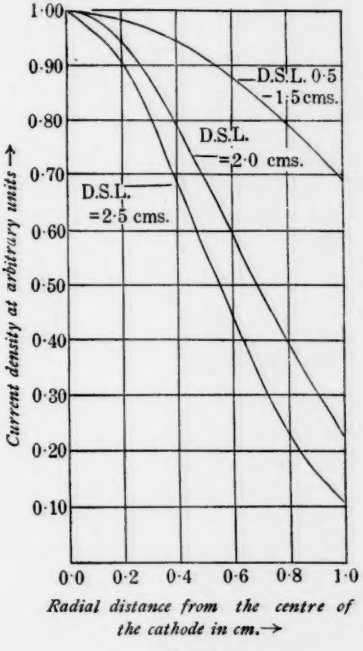

FIG. 4
Canal-Ray Discharge in Hydrogen
D.S.L. = Length of the cathode dark space

cathode surface in the case of hydrogen, as a function of the radial distance from the centre of the cathode surface, for different values of the D.S.L., under conditions of canal-ray discharge.

A variation of the earth current alters the relationship between the D.S.L. and the voltage across the discharge tube. It is possible, therefore, to study the radial distribution of the current for the same value of the D.S.L. but different values of the voltage. Such measurments have been made in the case of hydrogen and air for three different discharge currents 1·00, 1·60, 2·00, m.a. under conditions of both ordinary and canal-ray discharge. The results obtained in the case of hydrogen for conditions of ordinary discharge alone are shown in Tables 3–5. These observations indicate that for a given gas the radial distribution of the current-density on the cathode surface is independent of the voltage, of the discharge current and is only determined by the length of the cathode dark space. Thus for example in hydrogen with D.S.L. = 4 cms., and voltages of 2·5, 3·5 and 3·3 kV., the fractional currents over the first sector are 1·59, 1·49 and 1·45 and over the second sector, 0·12, 0·14 and 0·12 respectively, whereas, for the same applied voltage of 2·5 kV., when D.S.L. is 4·0 and 3·5 cms., the values over the first sector are 1·59 and 1·21 and over the second 0·12 and 0·20 respectively. Similar results are obtained in air.

§ 6. The differences in the current distributions in hydrogen and air under conditions of canal-ray and ordinary discharge are shown in Tables 5, 6 , 7, 8. Only in the case of hydrogen, the differences seem to be systematic. For instance in the case of the fractional current received by the first sector, the values obtained for conditions of canal-ray discharge are slightly but definitely smaller than those obtained under the conditions when there is no canal. In the case of air the differences observed are well within the limits of the experimental error. It is probable therefore that the central canal plays but a minor rôle in determining the radial distribution of the current on the cathode surface. We might have expected that the streaming of the high speed ions through the central canal, would have set up a pressure as well as an electrical gradient between the centre and the periphery, which would have affected the space-charge in such a manner as to have reduced the localisation. The results above indicate that such an effect if it exists is only of a secondary importance. In this connection one may mention a very interesting observation. A comparison of the results obtained in the case of the gases, air, hydrogen, oxygen and nitrogen under conditions of canal-ray discharge (Tables 6, 8–10) show that for the same value of the D.S.L. the fractional current-densities in the case of the different gases are the same. This does not apparently appear to hold good for the ordinary

conditions as will be seen from a perusal of the results obtained for air and hydrogen under these conditions. It may be pointed out that from the point of view of the influence of localisation on the intensity of the canal-ray beam the results obtained under the conditions of canal-ray discharge are more useful than those obtained under the ordinary conditions.

§ 7. The current received by any given area on the cathodic surface is made up of a number of parts.

1. The electron emission due to the photoelectric action.
2. The secondary electron emission due to bombardment with positive ions as well as neutral particles in the positive-ray beam.
3. The discharge of the positive ions on the cathode surface.

The observations on the radial distribution of the current on the cathodic surface can be interpreted in terms of the radial distribution among the impacting positive ions by making a few simplifying assumptions. These are :—

1. The effect due to the photoelectric action is distributed uniformly on the cathodic surface.
2. The intensity of the secondary electron emission is linearly proportional to the intensity of the primary rays.

   Such a relationship has been found by Bärwald[3] and more recently by Oliphant[3], in the case of a cold cathode, for impacting positive rays of energy less than one kilovolt. It is probable that the same relationship persists for the moderately high voltages of the order of five to six kilovolts used in these experiments.
3. The relative proportion of the charged to the uncharged particles in the vicinity of the cathode, does not vary in the radial direction. This assumption is necessary because the mechanism by which electron emission is brought about by impact with charged and neutral particles can be different. In the case of the former, for example, part of the emission could take place thorugh a mechanism similar to that responsible for the Schottkey effect[4], in other words that which is brought about when the electrons in the metal are subjected to the intense electric field of the impacting positive ions.

If we make these assumptions then the radial distribution of the current gives also the radial distribution among the impacting positive ions.

In the end I offer my grateful thanks to Prof. Dr. S. S. Joshi for giving me the facilities for work and constant encouragement. I also thank Prof. Dr. Asundi for discussion and helpful suggestions.

Summary

The radial distribution of the electric current on the cathodic surface has been investigated by observing the current distribution between the three sectors of a cathode in the case of the discharge in the gases oxygen, hydrogen, nitrogen and air for different voltages, discharge currents and lengths of the cathode dark space, under conditions of ordinary and canal-ray discharge.

The following results are obtained:—

1. There is in general a concentration of the current in the centre for the range of voltages used, in the case of the different gases.

2. For a given gas the localisation (or this concentration of the discharge) is independent of the voltage, the discharge current, and is determined only by the length of the cathode dark space (D.S.L.).

3. The localisation increases with the length of the cathode dark space and reaches a stationary value for very high lengths (of the order of 5 cms.).

4. Under the conditions of canal-ray discharge, the localisation is only slightly different from that obtained with an ordinary tube in the case of hydrogen. There is no such difference in the case of air. Under these conditions the radial distribution of the current-density is the same for the different gases for the same value of the D.S.L.

REFERENCES

1. W. Wien .. '*Kanal-strahlen*' *Handbuch der Experimental Physik*, 1927, pp. 767 and 437.
2. G. D. Yarnold and S. Holmes *Phil. Mag.*, 1936, **22**, 988.
3. H. Bărwald .. *Ann. d. Phys.*, 1919, **60**, 1.
   M. L. Oliphant .. *Proc. Roy. Soc.*, 1930, **127** A, 373.
4. ———— and Moon *Ibid.*, 1930, **127** A, 388.

RAMAN SPECTRUM OF SULPHUR

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1. Introduction

The infra-red and the Raman spectra of sulphur do not seem to have received a satisfactory interpretation till now, in spite of the fact that it is a common element. Krishnamurti[1] and Venkateswaran[2] are amongst those who have studied the Raman spectrum of this substance in the crystalline state. There is a fair agreement between the frequencies reported by these two authors as may be seen from Table II. Krishnamurti recorded seven Raman frequencies and Venkateswaran also recorded these and an additional frequency at 114. In all, eight frequencies had thus been recorded and Venkateswaran attributed one of these at 88 to the lattice and the remaining seven to the S_8 molecule. Bhagavantam and Venkatarayudu[3] calculated the normal frequencies of the sulphur molecule and they remarked that the line at 114 may also be attributed to the lattice. If such an interpretation is correct, there should be expected another fundamental at about 500. Their calculations lead to this conclusion.

The infra-red absorption of crystals of rhombic sulphur has been studied by Coblentz,[4] Schubert[5] and Taylor and Rideal[6] in the near infra-red region and by Barnes[7] in the far infra-red region. Krishnamurti has explained the near infra-red absorption maxima as combinations of two or more suitable fundamental frequencies. Venkateswaran attempted to identify all the observed far infra-red absorption maxima with one or other of the frequencies obtained in the Raman effect. Neither of these authors had taken into account the selection rules appropriate to the case of sulphur. It has been shown by Bhagavantam and Venkatarayudu that no correspondence between the infra-red absorption and Raman spectra need be expected in this case and we shall see later that only a limited number of combinations are permitted to appear in its infra-red absorption spectrum. In view of these discrepancies, it becomes necessary to revise the interpretation of the Raman and the infra-red absorption frequencies.

Accordingly, a detailed investigation of the Raman spectrum of a single crystal of rhombic sulphur is undertaken and a more satisfactory explanation of the infra-red absorption maxima is attempted in the present paper.

2. *Experimental*

Crystals of appreciable size have been grown by slow evaporation of a filtered solution of sulphur in carbon disulphide. A small flawless single crystal of rhombic sulphur is selected for the study. Light from a 6-inch quartz mercury arc lamp is condensed by means of an 8-inch glass condenser on to one face of the crystal. The scattered light emerging out from one of the other faces is focussed on the slit of a Fuess glass spectrograph with a suitable lens. With proper precautions, an intense and clear spectrum of sulphur has been obtained by giving an exposure of about twenty hours and this picture is reproduced in the accompanying plate. λ 5461 A.U. is used as the exciting radiation and Ilford Golden Isozenith plates are used to record the spectrum.

3. *Raman Spectrum of Sulphur*

The Raman frequencies obtained with a single crystal of rhombic sulphur are given in Table I.

TABLE I

Raman frequencies of sulphur

Wave-length of the Raman line A. U.	Wave number Cm.$^{-1}$	Exciting line A. U.	Raman shift Cm.$^{-1}$
5485·8	18224	5460·7	84
5495·1	18193	,,	115
5507·4	18152	,,	156
5516·3	18123	,,	185
5526·1	18091	,,	217
5532·7	18069	,,	239
5595·1	17868	,,	440
5606·0	17833	,,	475
5620·1	17788	,,	520
5435·9	18391	,,	− 83
5426·9	18422	,,	−114

$\Delta\nu$ = 84, 115, 156, 185, 217, 239, 440, 475, 520.

The Raman frequencies of rhombic sulphur obtained by the author are compared with those obtained by the earlier workers in Table II. An

TABLE II

Raman frequencies of sulphur compared with earlier observations

Krishnamurti	85 (med. st).	..	152 (*st*)	183 (*w*)	216 (*st*)	243 (*w*)	434 (*w*)	470 (*st*)	..
Venkateswaran	88 (5)	114 (0)	152 (10)	185 (0, *d*)	216 (10)	243 (1, *d*)	434 (2, *d*)	468 (10)	..
Author	84 (5)	115 (5)	156 (10)	185 (1, *d*)	217 (10)	239 (1, *d*)	440 (2, *d*)	475 (7)	520 (0)

extremely faint line at 520 has been recorded here for the first time. The numbers in the brackets represent the relative intensities.

The Raman line at 114 has been recorded by Venkateswaran as a faint line whereas it is quite intense in the author's pictures.

4. *Effect of Temperature*

A rhombic crystal was mounted inside an electric heater provided with suitable windows. The temperature of the crystal was gradually raised to 105° C. where it was kept constant. It is expected, as has been shown by Bech and Ebbinghaus,[8] that the monoclinic variety is obtained in this way at 105° C. The Raman spectrum of sulphur has been photographed under these conditions and also at the room temperature on the same plate by using a Hartmann diaphragm to ascertain whether there is any shift in the lines or not. No change, either in the frequency or in the relative intensities of the Raman lines, could be observed.

Venkateswaran has, however, recorded that the line at 88 of rhombic sulphur is shifted to 80 in the case of monoclinic sulphur at 110° C. Sirkar and Gupta[9] also studied the Raman spectra of rhombic and monoclinic varieties of sulphur but they reported that no change has been observed to take place in the position of the lines with the transformation from the rhombic to the monoclinic variety.

5. *Effect of Crystal Orientation*

In the case of a uniaxial crystal, if we designate the direction of the incident light by OX, that of the scattered light by OY and the vertical line by OZ, three alternatives arise in respect of the nature of the incident light. It may be unpolarized or linearly polarized along OZ or linearly polarized along OY. In each case, the optic axis of the crystal may be placed parallel to either OX or OY or OZ. Thus the number of alternative arrangements becomes nine. For each one of these settings, the scattered light may either be photographed as such or only the horizontal component of it or only the

vertical component of it may be photographed, thus enabling the observer to secure 27 separate spectra on the whole. In the case of rhombic sulphur, which is a biaxial crystal, the number will obviously become 54. It may easily be seen that only 24 of these, obtained by analysing both the incident and the scattered beams, are the most important ones. These 24 spectrograms have been obtained by the author in the present investigation with a good crystal of sulphur.

Light from a quartz mercury lamp is focussed on the crystal by a large glass condenser involving a semi-angle of convergence of about 10°. A suitably oriented polaroid disc is used for securing the desired state of polarization for the incident light. The scattered light is separated into the horizontal and the vertical components by means of a suitably oriented double image prism and the two components are simultaneously photographed. On account of the fact that the crystal used is not a big one and that a polaroid has been employed, it is thought that the results obtained cannot be deemed to have a quantitative significance and are not, therefore, extensively quoted here. Only the main features are recorded.

The important conclusions, arrived at after a careful examination of the plates, relate to: (i) the reciprocal behaviour of the total symmetric and the degenerate oscillations and (ii) the existence of two preferred orientations, namely, those in which both the direction of the incident light vector and the orientation of the C-axis are along OZ. In these two cases, the total symmetric oscillations come out very strongly. This is apparently due to the fact that the plane of the sulphur ring is parallel to the C-axis and we have to conclude that the total symmetric oscillations are excited more strongly when the incident light vector is parallel to the plane of the ring than when it is perpendicular to it. The reciprocal behaviour of the total symmetric oscillations on the one hand and the degenerate oscillations on the other is also expected and this result is analogous to the observations made by Nedungadi[10] in $NaNO_3$ and Bhagavantam[11] in calcite.

6. *Discussion of the Raman Spectrum and Infra-red Absorption*

From the X-ray studies of rhombic sulphur, Mark and Wigner[12] concluded that the unit cell contains 128 atoms grouped as eight molecules of sixteen atoms each. Taylor and Rideal extended that view by postulating that the S_{16} molecule consists of 8 (S_2) groups which are situated at the corners of the cube. Contrary to these findings, Warren and Burwell[13] concluded from similar studies that rhombic sulphur belongs to the space group V_h^{24} and that the unit cell contains sixteen S_8 molecules. The atoms in each molecule are located at the corners of a puckered octagon made up

of two equal squares one turned through 45° with respect to the other. The planes of the two squares are parallel but not coincident. From the intensity measurements, they found that the plane of the ring is parallel to the C-crystallographic axis and makes an angle of about 50° with the *a*-axis.

Assuming the model suggested by Warren and Burwell, Bhagavantam and Venkatarayudu[14] calculated the normal frequencies of sulphur molecule by applying the group theoretical methods. Out of the eleven vibrational frequencies that are to be expected, only seven are active in Raman effect, three others are active in infra-red absorption and one frequency is inactive in both. Of the nine frequencies obtained by the author, the two at 84 and 115 are now attributed to the lattice and the remaining seven are identified as the fundamental frequencies of the S_8 molecule. The fundamental frequencies obtained by the author are compared with those calculated by Venkatarayudu[15] in Table III.

TABLE III

Comparison between the observed and the calculated frequencies

Number	Class	Frequency calculated Cm.$^{-1}$	Frequency Observed in Raman effect Cm.$^{-1}$	Frequency observed in infra-red absorption Cm.$^{-1}$
ν_1	A_1	470	475	*f*
ν_2	,,	216	217	*f*
ν_3	B_1	400	*f*	400 (*w*)
ν_4	B_2	359	*f*	*f*
ν_5	E_1	456	*f*	465 (*st*)
ν_6	,,	203	*f*	200 (*st*)
ν_7	E_2	482	520	*f*
ν_8	,,	196	185	*f*
ν_9	,,	113	156	*f*
ν_{10}	E_3	454	440	*f*
ν_{11}	,,	243	239	*f*

f denotes that the line is forbidden from appearing. The three fundamental infra-red absorption maxima that are to be expected and that have been observed are also given in the last column of the above table.

Of these, ν_1 and ν_2 come under the total symmetric class and the rest are degenerate. The two possible symmetrical vibrations are (1) that in which the two squares are vibrating against each other and (2) that in which the four atoms in each square move towards or away from the centre of the square. The first mode of oscillation takes place in a direction parallel to the symmetry axis and Venkateswaran has given sufficient reasons to consider the frequency at 217 as the one arising out of such oscillations. Hence, the second one at 475 which is intense, sharp and well polarized, should be attributed to the expansions and contractions of the squares constituting the molecule.

The unit cell of rhombic sulphur contains sixteen molecules of eight atoms each. A complete analysis of its normal modes would be very difficult of achieving. Bhagavantam and Venkatarayudu[16] have shown that when a group of atoms constituting an ion or molecule goes to build up a crystal, its normal modes usually undergo three types of modification, namely, splitting of degenerate vibrations, multiplicity due to the unit cell containing more than one molecule and alteration in selection rules. It is, however, a matter of experimental fact that none of the Raman lines which are forbidden in the case of the sulphur molecule have appeared in the crystal nor has any splitting been observed. We may therefore regard the selection rules applicable to a molecule to be valid in the case of the crystal also both in Raman effect and infra-red absorption.

The character table and the selection rules derived by Bhagavantam and Venkatarayudu in the case of sulphur molecule reveal that only three fundamental frequencies should appear in the infra-red absorption and that there should be no correspondence between the Raman lines and the infra-red absorption maxima. Barnes has studied the infra-red absorption of rhombic sulphur crystal in the far infra-red region and he recorded maxima at $<$ 77, 87, 104, 149, 200–250, 267, 400 and 465. Of these, the three peaks at 149, 200 and 465 are strong absorptions. The three infra-red fundamentals in the case of sulphur have already been taken as 200, 400 and 465. The frequencies at $<$ 77, 87 and 104 can be taken as those due to the lattice. The remaining two frequencies observed by Barnes and also the four maxima observed by Taylor and Rideal in the near infra-red region at 685, 840, 932 and 1289 have to be explained either as overtones or combinations with due regard to the selection rules.

Following the selection rules for the combinations and overtones given by Tisza,[17] a detailed scheme for their appearance or otherwise has been worked out. The selection rules for the overtones in the infra-red absorption

are given in Table IV. *f* and *p* denote respectively that the line is forbidden or permitted to appear.

TABLE IV

Selection rules for the overtones in the infra-red absorption of sulphur

Class	Fundamental	First overtone	Second overtone
A_1	*f*	*f*	*f*
A_2	*f*	*f*	*f*
B_1	*p*	*f*	*p*
B_2	*f*	*f*	*f*
E_1	*p*	*f*	*p*
E_2	*f*	*p*	*p*
E_3	*f*	*f*	*p*

The selection rules for the combinations are given in Table V. Combinations which are permitted in the infra-red absorption are printed in bold type. For example, a frequency coming under the class B_1 can combine with one coming under either E_3 or A_1 only. In the former case, the combination will have the characters of the representation E_1 and in the latter it will have those of B_1. Accordingly, these combinations are permitted in the infra-red absorption.

TABLE V

Selection rules for the combinations in the infra-red absorption of sulphur

Class	A_1	A_2	B_1	B_2	E_1	E_2	E_3
A_1	A_1	A_2	$\mathbf{B_1}$	$\mathbf{B_2}$	$\mathbf{E_1}$	E_2	E_3
A_2		A_1	$\mathbf{B_2}$	$\mathbf{B_1}$	$\mathbf{E_1}$	E_2	E_3
B_1			A_1	A_2	E_3	E_2	$\mathbf{E_1}$
B_2				A_1	E_3	E_2	$\mathbf{E_1}$
E_1					$A_1+A_2+E_2$	$\mathbf{E_1+E_3}$	$\mathbf{B_1+B_2+E_2}$
E_2						$\mathbf{A_1+A_2+B_1+B_2}$	$\mathbf{E_1+E_3}$
E_3							$A_1+A_2+E_2$

A detailed scheme, interpreting all the observed infra-red frequencies, is given in Table VI.

TABLE VI

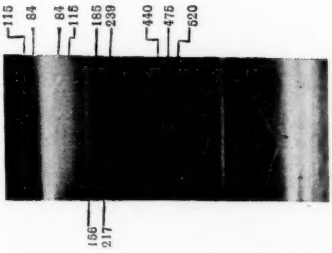
Interpretation of the observed infra-red frequencies

Number	Observed frequency Cm.$^{-1}$	Assignment due to the author	Calculated value only for combinations and overtones Cm.$^{-1}$
1	< 77	lattice frequency	..
2	87	,,	..
3	104	,,	..
4	149	Overtone of < 77	..
5	200	ν_6	..
6	267	$2\,\nu_9$	312
7	400	ν_3	..
8	465	ν_5	..
9	685	$\nu_5 + \nu_2$	682
10	840	$\nu_3 + \nu_{10}$	840
11	932	$\nu_1 + \nu_5$	940
12	1289	$3\,\nu_{10}$	1320

It is needless to add that most of the assignments given by the earlier authors are not in agreement with the selection rules.

7. *Summary*

The complete Raman spectrum of a single crystal of rhombic sulphur has been obtained. Nine frequencies at 84, 115, 156, 185, 217, 239, 440, 475 and 520 cm.$^{-1}$ have been recorded. Of these, the two frequencies at 84 and 115 have been attributed to the lattice and the remaining seven frequencies are taken as the fundamentals appropriate to the S_8 molecule. Out of the eight infra-red absorption maxima recorded by Barnes, the three at 200, 400 and 465 cm.$^{-1}$ are attributed to the molecule. Three others at < 77, 87 and 104 are attributed to the lattice. The other two frequencies observed by Barnes at 149 and 265 and the four infra-red absorption maxima recorded by Taylor and Rideal at 685, 840, 932 and 1289 cm.$^{-1}$ are explained as



Raman Spectrum of Sulphur

suitable combinations or overtones. A detailed scheme showing the selection rules for the occurrence of overtones and combinations in the infra-red absorption has been given.

The Raman spectrum of sulphur has been studied at 30° C. and 150° C. but no change either in the relative intensities or in the position of the lines has been observed. The effect of crystal orientation on the Raman spectrum has also been studied. It has been found that the total symmetric oscillations behave in a manner which is reciprocal to that of the degenerate oscillations.

In conclusion, the author desires to express his grateful thanks to Prof. S. Bhagavantam for the keen interest he has shown during the progress of this work.

REFERENCES

1. Krishnamurti .. *Ind. J. Phys.*, 1930, **5**, 105.
2. Venkateswaran .. *Proc. Ind. Acad. Sci.*, 1936, **4**, 345.
3. Bhagavantam and Venkatarayudu .. *Ibid.*, 1938, **8**, 115.
4. Coblentz .. *Investigations of Infra-red Spectra*, 1905, **1**, 66.
5. Schubert .. *Diss. Breslau.*, 1916.
6. Taylor and Rideal .. *Proc. Roy. Soc.*, 1927, **115**, 589.
7. Barnes .. *Phy. Rev.*, 1932, **39**, 562.
8. Bech and Ebbinghaus .. *Berichte deut. chem. Ges.*, 1906, **29**, 3870.
9. Sirkar and Gupta .. *Ind. J. Phys.*, 1937, **10**, 473.
10. Nedungadi .. *Proc. Ind. Acad. Sci.*, 1939, **10**, 197.
11. Bhagavantam .. *Ibid.*, 1940, **11**, 62.
12. Mark and Wigner .. *Z. Phys. Chem.*, 1924, **111**, 398.
13. Warren and Burwell .. *Jour. Chem. Phy.*, 1935, **3**, 6.
14. Bhagavantam and Venkatarayudu *Proc. Ind. Acad. Sci.*, 1938, **8**, 101.
15. Venkatarayudu .. *Thesis submitted to the Andhra University*, 1940.
16. Bhagavatnam and Venkatarayudu *Proc. Ind. Acad. Sci.*, 1939, **9**, 224.
17. Tisza .. *Z. f. Phys.*, 1933, **82**, 48.

ON THE EXPANSION OF AN ARBITRARY FUNCTION IN A SERIES OF EIGENFUNCTIONS OF BOUNDARY VALUE PROBLEMS

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Let D be a bounded open domain, simply or multiply connected, whose boundary C is composed of a finite number of regular curves in the x, y plane, and let $\omega_n(x, y)$ be the eigenfunctions (normal and orthogonal) with the corresponding eigenvalues $\lambda_n > 0, n: 1, 2, \ldots$ of the boundary value problem

$$\Delta \omega + \lambda \omega = \frac{\partial^2 \omega}{\partial x^2} + \frac{\partial^2 \omega}{\partial y^2} + \lambda \omega = 0 \tag{1}$$

$$\omega (x, y) = 0 \qquad \text{on C.} \tag{2}$$

We assume that the eigenvalues λ_n have been arranged in increasing order of magnitude. The object of this note is to prove the following:

Theorem A. Let $f(x, y)$ be a bounded measurable function defined in D + C and let

$$f(x, y) \sim \Sigma a_n \omega_n (x, y) \tag{3}$$

where

$$a_n = \int_D f(x, y) \omega_n (x, y) \, dx \, dy \tag{4}$$

Then at a point (x, y), interior to D, where $f(x, y)$ is continuous

$$\lim_{t \to +0} \sum_{n=1}^{\infty} a_n \omega_n (x, y) e^{-\lambda_n t} \tag{5}$$

exists and is equal to the value of the function at the point.

We will in fact be proving more than theorem A. If C_δ denotes a circle in D with centre (x, y) and radius $\delta > 0$ and if

$$f_\delta (x, y) = \frac{1}{\pi \delta^2} \int_{C_\delta} f(\xi, \eta) \, d\xi \, d\eta \tag{6}$$

then, $\lim_{\delta \to 0} f_\delta (x, y)$, if it exists, is called the '*mean limit*' of $f(x, y)$ at the point (x, y), and (x, y) is called a point of '*mean continuity*', if $f(x, y) = \lim_{\delta \to 0} f_\delta (x, y)$. We have then the following generalisation of Theorem A.

THEOREM B. At a point of mean continuity of $f(x, y)$ or even at a point (x, y) in D, where the mean limit of $f(x, y)$ exists,

$$\lim_{t \to +0} \sum_{n:1}^{\infty} a_n \omega_n (x, y) e^{-\lambda_n t} \tag{5}$$

exists and is equal to the mean limit of $f(x, y)$.

This theorem is apparently an analogue of Poisson's theorem in the theory of Fourier series, and suggests the possibility of associating a summation process involving the eigenvalues λ_n corresponding to the eigenfunctions $\omega_n (x, y)$ to the Fourier series on the right of (3). Can it be said for example, that at a point (x, y) where $f(x, y)$ is continuous, the Fourier series of $f(x, y)$ is summable (R, λ, 1) to $f(x, y)$, that is,

$$\lim_{T \to \infty} \sum_{\lambda_n \leqslant T} \left(1 - \frac{\lambda_n}{T}\right) a_n \omega_n (x, y) = f(x, y) \; ? \tag{7}$$

This problem remains open, but it is pointed out here that the Fourier series of $f(x, y)$ is summable by a process that includes (R, λ, 1) process.

In so far as a point of continuity of $f(x, y)$ is also a point of mean continuity, it is sufficient to prove Theorem B, the proof of which is only briefly indicated, as this theorem, with a detailed proof will be included in a memoir to be published later on.

Proof of Theorem B.—It is known[1] that if $\omega (x, y)$ is a solution of (1), then

$$\begin{aligned} \omega_\rho (x, y) &= \frac{1}{\pi \rho^2} \int_{C_\rho} \omega (\xi, \eta) \, d\xi \, d\eta \\ &= 2 \frac{J_1 (\rho \sqrt{\lambda})}{\rho \sqrt{\lambda}} \omega (x, y). \end{aligned} \tag{8}$$

If we put $\phi (x, y) = \dfrac{1}{\pi \rho^2}$ in C_ρ and O outside C_ρ, we see by Parseval's formula

$$\frac{1}{\pi \rho^2} \int_D f(\xi, \eta) \phi (\xi, \eta) \, d\xi \, d\eta = f_\rho (x, y) = \sum_{n=1}^{\infty} a_n \omega_n (x, y) \cdot 2 \cdot \frac{J_1 (\rho \sqrt{\lambda_n})}{\rho \sqrt{\lambda_n}} \tag{9}$$

the series on the right converging for all $\rho > 0$, such that $C_\rho \subset D$. Let us set

$$\left.\begin{aligned} C_n &= a_n \omega_n (x, y) \\ \alpha_\mu (\theta) &= 2^\mu \Gamma (\mu + 1) \frac{J_\mu (\theta)}{\theta^\mu}, \mu > 0 \\ \phi_\mu (\rho) &= \sum_{n=1}^{\infty} C_n \alpha_\mu (\rho \sqrt{\lambda_n}) \end{aligned}\right\} \tag{10}$$

[1] A. Hammerstein, "Uber Entwicklungen gegebener Funktionen nach Eigenfunktionen von Randwertaufgaben," *Math. Zeitscr.*, 1928, **27**, 269–311, formula (17).

so that $\phi_1(\rho) = f_\rho(x, y)$. Here $J_\mu(\theta)$ denotes the Bessel function of order μ.

At a point where the mean limit of $f(x, y)$ exists, $\phi_1(\rho)$ tends to a limit as $\rho \to 0$. Using known asymptotic values of C_n and $J_\mu(\theta)$ we see that there exists $a/\mu > 1$[2], such that $\phi_\mu(\rho)$ is defined for all $\rho > 0$, the series for $\phi_\mu(\rho)$ being absolutely convergent. For such a μ and small ρ.

$$\phi_\mu(\rho) = 2\mu(\mu-1)\int_0^1 \phi_1(\rho t)\, t^3 (1-t^2)^{\mu-2}\, dt \qquad (11)^3$$

This shows that if $\lim_{\rho \to 0} \phi_1(\rho)$ exists, then $\lim_{\rho \to 0} \phi_\mu(\rho)$ also exists and is equal to the former limit. Since $\phi_\mu(\rho)$ exists for all $\rho > 0$, we see that the integral

$$F(t) = \frac{2}{(4t)^{\mu+1}\,\Gamma(\mu+1)} \int_0^\infty \rho^{2\mu+1} e^{-\frac{\rho^2}{4t}}\, \phi_\mu(\rho)\, d\rho \qquad (12)$$

exists for $t > 0$, and it is a simple Abelian result that

$$\lim_{t \to +0} F(t) = \lim_{\rho \to +0} \phi_\mu(\rho). \qquad (13)$$

whenever the limit on the right exists. Now if we substitute the expression in series for $\phi_\mu(\rho)$ on the right of (12) and integrate term by term, which can be seen to be permissible, we observe that[4]

$$F(t) = \Sigma C_n\, e^{-\lambda_n t}$$

$$= \sum_{n:1}^{\infty} a_n\, \omega_n(x, y)\, e^{-\lambda_n t} \qquad (14)$$

for $t > 0$. This proves Theorem B.

Remarks.—(i) Theorem A shows that for a bounded measurable function $f(x, y)$

$$\lim_{t \to 0} \Sigma\, a_n\, \omega_n(x, y)\, e^{-\lambda_n t} = f(x, y) \qquad (15)$$

almost everywhere in D. If the measurable function $f(x, y)$ is unbounded but integrable L^p, $p \geqslant 1$, then using a theorem of Kolmogoroff[5] to the effect

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[2] $J_\mu(\theta) = O\left(\frac{1}{\sqrt{\theta}}\right)$ as $\theta \to +\infty$. G. N. Watson, *Bessel Functions*, p. 195. Using the same argument as in Watson, *loc. cit.*, p. 637, we show that $C_n = O(\lambda_n^{\frac{3}{4}})$ and then the existence of a $\mu > 1$ follows since $\sum_1^\infty \frac{1}{\lambda_n^2} < \infty$.

[3] F. Bowman, *Bessel Functions*, p. 98.

[4] Watson, *loc. cit.*, p. 394, formula (4).

[5] A. Kolmogoroff, "Uber kompaktheit der Funktionenmemgem bei der Konvergenz in Mittel", *Gottinger Nachrichten*, 1931, pp. 60–63.

that

$$\lim_{\delta \to 0} \int_{D} |f(x, y) - J_{\delta}(x, y)|^{p} \, dx \, dy = 0 \tag{16}$$

it can be shown on setting

$$U(x, y, t) = \sum_{1}^{\infty} a_n \, \omega_n(x, y) \, e^{-\lambda_n t} \tag{17}$$

where $$f(x, y) \sim \Sigma \, a_n \, \omega_n(x, y) \tag{3}$$

that $$\lim_{t \to 0} \int_{D} |f(x, y) - U(x, y, t)|^{p} \, dx \, dy = 0 \tag{18}$$

which shows that the relation (15) still persists almost everywhere in **D**.

(ii) Theorems A and B remain true in space of n-dimensions as well. We have only to replace the circle C_{δ} by a sphere in n-dimensions.

(iii) The same theorems hold good in the case of second and third boundary value problems as well, because whatever the boundary conditions the relation (8) remains true.

(iv) Let $K(x, y; \xi, \eta)$ be a symmetric kernel defined in **D** fulfilling the following properties of Green's function

(α) $K(x, y; \xi, \eta)$ is of the form

$$-\frac{1}{2\pi} \log r + \gamma(x, y; \xi, \eta)$$

where $r = \{(x - \xi)^2 + (y - \eta)^2\}^{\frac{1}{2}}$ and $\gamma(x, y; \xi, \eta)$ has continuous derivatives of first two orders and

(β) $$\Delta_{\xi, \eta} K(x, y; \xi, \eta) = 0.$$

Then[6] if $\phi_n(x, y)$ are the eigenfunctions of $K(x, y; \xi, \eta)$ with the corresponding eigenvalues λ_n, which are positive,

$$\Delta \phi_n(x, y) + \lambda_n \phi_n(x, y) = 0.$$

Hence theorems A and B continue to remain true for such eigenfunctions as well.

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[6] A. Hammerstein, *loc. cit.*, § 6.

CHEMICAL INVESTIGATION OF INDIAN LICHENS

Part I. Chemical Components of *Roccella montagnei*

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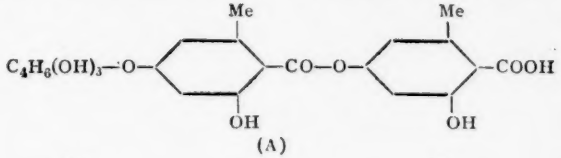
THE lichens, known as *Sailaja* in Sanskrit, *Charila* in Hindi, *Kalpasi* in Tamil and *Rathipuchi* or *Rathipavvu* in Telugu, have excited a good deal of interest as regards their biological nature, botanical classification and chemical composition. They are chiefly found on the barks of trees and on rocks, and are very slow growing plants representing a symbiosis between fungi and algæ. Their growth is dependent upon the humidity of the atmosphere and in general they are widely distributed over the surface of the globe. Being exceedingly diversified in their form, appearance and texture, more than three thousand species of them have been recorded by the botanists. They have found use in various ways as dye-stuffs (orchil, cudbear and litmus), food-stuffs and as material for making drugs. Excepting the work of Chopra[1] on the lichens of the Sikkim Himalayas, no detailed information is available about the distribution in India of the numerous species of lichens of economic importance. Watt[2] has recorded that the true Orchil (*Roccella tinctoria*) was to be found in Ceylon on the stems of certain palms, and that samples of this material were sent to the colonial and Indian exhibition (1886) as a drug from Madras. However, no knowledge appeared to exist of its value as a dye. An allied species (*Roccella fuciformis*) was recorded by Lindsay[3] as growing on the mango trees at Pondicherry.

The lichen, *Roccella montagnei*, occurs in abundance in Waltair and the neighbourhood and is chiefly found on the cashewnut, mango, pongamia, tamarind and banyan trees. The identification was made by sending a sample to Kew and we are thankful to the Director of that herbarium for it.

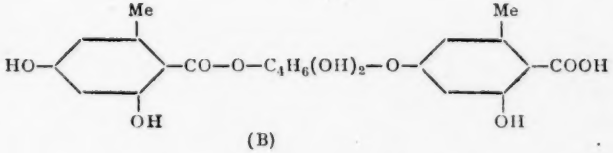
Hesse[4] was the first to examine a sample of this lichen obtained from Angola and he isolated from it erythrin and oxyroccellic acid. Subsequently Ronceray[5] detected the presence of orcinol also. Erythrin was, however, found to be the main component. The methods that they employed could not yield complete information regarding the composition of the lichen. A thorough examination of the Indian sample has now been made using a series of solvents in succession for purposes of extraction. Further, a number of samples obtained during different parts of the year and from different trees have also been analysed.

As a result of this investigation it has been found that the important components of this lichen are: Erythrin, Erythritol, Lecanoric acid, Orcinol and Roccellic acid. Of these, previous investigators did not obtain erythritol, lecanoric acid and roccellic acid. Oxyroccellic acid, which Hesse claimed to have isolated from the Angola sample, could not be found in the course of our work. Its place has possibly been taken up by roccellic acid. Samples collected from various trees were found to be very similar, but considerable variation in composition was noticed in samples obtained in different parts of the year.

During the years 1938 and 1939 about ten samples in all were extracted. Two typical cases are described in the experimental part. It was noticed that whenever erythrin was available in large quantity lecanoric and roccellic acids were absent and only small quantities of erythritol were obtained, and when lecanoric acid was found to be present it was accompanied by considerable quantities of erythritol and very little of erythrin. For obtaining good yields of erythrin samples collected during the wet months were found to be the best. These statements may not hold good always. But the details of the occurrence of erythrin and lecanoric acid along with erythritol in *Roccella montagnei* are highly interesting. They indicate that these two compounds are closely related. Of the two alternative formulæ (A)[6] and (B)[7] for erythrin both satisfy all known reactions and properties of the compound and there has been no unequivocal evidence in support of any one to the exclusion of the other. But the facts mentioned above lend support to formula (A) in which it is represented as the erythrityl ether of lecanoric acid. Work is in progress with a view to establish the constitution definitely.



(A)



(B)

Experimental

Two representative extractions of the lichen are described below. At the beginning the following series of solvents were employed in succession: light petroleum, benzene, ether, acetone, alcohol and water. Since it was

found that benzene and ethyl alcohol did not extract any appreciable quantity they were left out.

Extraction I: *Erythrin, Erythritol and Orcinol.*—The fresh lichen obtained from the trees was dried in the sun and ground into coarse powder in a coffee-mill. The extraction was carried out in a Soxhlet extractor designed to take up about 1 kilogram of the material, and the process was carried out first with light petroleum (60–80°) for about 24 hours. After removing the solvent from this extract, a residue amounting to 1·3% of the weight of the lichen was obtained. This consisted mostly of fatty and waxy matter along with carotene and xanthophyll. This was not further investigated. The fat-free lichen powder was then extracted with ether for 24 hours and subsequently with acetone for 48 hours. These extracts were separately examined as described below:

The ether extract amounted to 1·4% and consisted of a semi-solid mass. Part of it dissolved in water and after filtration a pale yellow crystalline solid was left behind. It could be readily recrystallised from acetone and was obtained in the form of bundles of pale yellow needles melting at 156–57°. (Found: C, 54·6; H, 5·6; $C_{20}H_{22}O_{10}$, H_2O requires C, 54·5; H, 5·5%.) This substance gave an orange-red colour with bleaching powder and an alcoholic solution of it turned violet on the addition of a drop of ferric chloride solution while with an excess of the reagent it turned reddish brown. From all these reactions it was identified as erythrin. The water-soluble portion was recovered by the concentration of the aqueous extract. It dissolved easily in ether, alcohol and water and gave all the reactions of orcinol. It gave a deep violet colour with ferric chloride and the characteristic homofluorescein reaction with chloroform and alkali. But the sample was contaminated with a tenacious impurity which rendered purification extremely difficult and wasteful. The yield of the crude orcinol was about 0·3%.

The acetone extract, amounting to about 7·5% of the lichen, was also a sticky mass. It could be divided into two portions by treatment with water. The water-insoluble portion was separated by filtration and washing with small quantities of water. It was readily recrystallised from acetone and was found to be erythrin by comparison with the sample obtained from the ether extract. The aqueous extract yielded a semi-solid mass on concentration and drying in a desiccator. When treated with a little ether a white crystalline solid separated out. This was filtered and washed with small quantities of ether. When recrystallised from alcohol, it came out as large colourless hexahedral crystals melting at 122°. It possessed a sweet taste. (Found: C, 39·6; H, 8·0; $C_4H_{10}O_4$ requires C, 39·3; H, 8·2%.)

t was therefore concluded to be erythritol and the identification was confirmed by the preparation of the benzoyl derivative melting at 185–86°, the acetyl derivative melting at 86°, and the formate melting at 150–51°. The ether extract gave rise to a little orcinol on evaporation.

The residual lichen powder was finally boiled with water for 48 hours and the aqueous extract concentrated. This gave no colouration with ferric chloride and a blue colour with iodine. It reduced twice the amount of Fehling's solution after hydrolysis with hydrochloric acid than before hydrolysis, was insoluble in ammonio-copper sulphate solution and gave no acetyl derivative. It was therefore identified as isolichenin.

The yields of the pure crystalline compounds obtained from this sample of lichen were as below: erythritol 2·0 % and erythrin 5·3%.

Extraction II: *Roccellic acid, Erythritol, Lecanoric acid and Orcinol.*— The light petroleum extract was just the same in quantity and composition as in the case of sample (1). The ether extract (yield 1·0%) was treated with water just as before and the water-insoluble solid recrystallised from acetone. The substance thus obtained was in the form of colourless rectangular rods and melted at 132–33°. (Found: C, 67·5; H, 10·7; $C_{17}H_{32}O_4$ requires C, 68·0; H, 10·6%.) It was soluble in benzene, acetone, ether and alcohol and very sparingly soluble in water. $[\alpha]_D$ in ethyl alcohol $= +17·6°$. It was an acid by nature dissolving readily in sodium bicarbonate solution and gave no colour with bleaching powder or with ferric chloride in alcoholic solution. Similar to succinic acid it gave the fluorescein reaction when fused with resorcinol. In view of all these properties the compound was identified as roccellic acid.

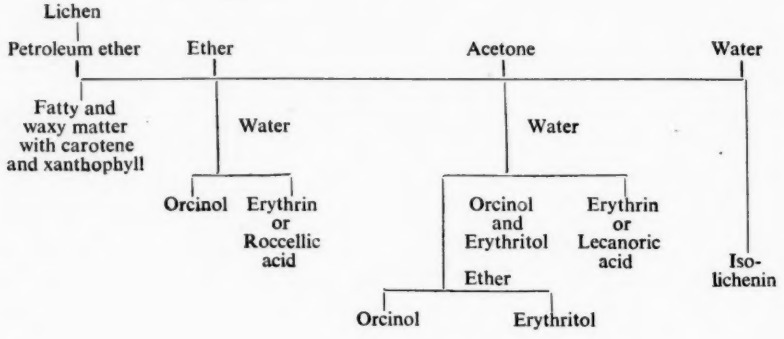
During the course of the extraction of the lichen with acetone erythritol began to separate out in the form of large crystals in the receiver. After 48 hours when the extraction was found to be over it was removed by filtration and subsequently washed with small quantities of acetone. The acetone solution was then distilled in order to recover the solvent and the residual amorphous solid treated with water. A highly coloured solid was left undissolved. The aqueous solution was found to contain some more erythritol and orcinol and these were recovered by evaporating the solution and treating the residue with ether as has already been described. The purification of the coloured water-insoluble solid was effected as follows: It was dissolved in the minimum quantity of acetone and diluted with an equal volume of water when a precipitate consisting mostly of colouring matter separated out immediately. It was filtered off, the filtrate diluted with a large quantity of water and repeatedly extracted with ether. On evaporating the ether

solution a yellow solid was obtained which crystallised from acetone as pale yellow elongated needles melting at 166° with decomposition. Further purification was effected by dissolving the substance in the minimum quantity of acetone-ether mixture (1 : 1) and adding to it benzene or chloroform. An amorphous solid that first separated out was removed and subsequently colourless needles of lecanoric acid were formed. The melting point now went up to 173–74° (decomp.). The substance gave a blood-red colour with bleaching powder and a stable violet colour with ferric chloride and agreed closely in all respects with an authentic sample of the acid and the mixed melting point was undepressed.

Final extraction of the lichen with boiling water yielded isolichenin as before.

The yields of the different crystalline compounds were (1) Roccellic acid 0·8%, (2) Erythritol 3·5% and (3) Lecanoric acid 1·0%.

The following table summarises the processes adopted for the separation of the various components of the lichen:



Summary

The lichen *Roccella montagnei* collected in Waltair has been found to differ markedly in composition, depending upon the season. Erythrin, Erythritol, Lecanoric acid, Roccellic acid and Orcinol are the main components besides isolichenin. The present findings differ from previous work in that erythritol and roccellic acid are now found in this lichen whereas oxyroccellic acid is absent. The constitution of erythrin as the erythrityl ether of lecanoric acid is supported.

REFERENCES

1. Chopra .. *Lichens of Sikkim Himalayas* (Punjab University Press).
2 and 3. Watt .. *A Dictionary of Economic Products of India*, **4**, 636.
4. Hesse .. *J. Pr. Chem.*, 1898, (ii), **57**, 232.
5. Ronceray .. *Bull. Soc. Chim.*, 1904, (iii), 1097.
6. Hesse .. *Ber.*, 1904, **37**, 4693.
7. Zerner .. *Monatsh.*, 1914, **35**, 1021.

WAX FROM *BUTEA FRONDOSA* FLOWERS

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Butea frondosa flowers are well known for their use as a dye-stuff and they are also said to possess medicinal properties. For our studies on these flowers we had occasion to collect them in large quantities during the last three years and subject them to a preliminary treatment to remove the fatty and waxy matter. We found that light petroleum ether removes the waxy matter completely along with some chlorophyll and on further purifying the petroleum ether extract a colourless solid wax (yield 0·75% and m.p. 73–76°) was obtained. However during the last season we used for the preliminary purification carbon tetrachloride in the place of light petroleum ether. On further purifying the extract a colourless wax having the same physical and chemical properties as the previous one was obtained in 0·35% yield. This clearly indicated the existence of a definite waxy matter (m.p. 73–76°) in the flowers, though the yield might vary according to the method adopted or the ripeness of the flowers and seasonal variations.

The unsapoinifiable matter of the wax consisted mostly of myricyl alcohol and a very small quantity of a substance probably belonging to the steroid group and giving a bluish-green colour in Liebermann-Burchard reaction. The composition of the acid part seems to be interesting since it was composed mostly of higher saturated acids. The quantities of acids obtained were too small to be separated by fractional distillation and hence crystallisation methods were adopted to separate and characterise them. By repeated fractional crystallisations from different solvents three definite fractions (1) m.p. 76–78°, M.W. 380, (2) m.p. 72–74°, M.W. 350, (3) m.p. 62–64°, M.W. 275 were obtained. From the melting points and the mean molecular weights of these fairly definite fractions, it can be seen that the fraction (1) may be a mixture of cerotic and lignoceric acids, the fraction (2) may be a mixture of arachidic and lignoceric acids and the fraction (3) that of palmitic and stearic acids.

Manjunath *et al*[1] working on the *Butea frondosa* seed oil obtained these higher saturated acids and found it impossible to separate them completely and drew their conclusions from the melting point—molecular weight curves

of mixtures of pure acids. They obtained two definite fractions, in addition to other acids, one melting at 74·5–75·5° with a M.W. 253 and the other melting at 77·5–79° with a M.W. 383 and suggested that they might be eutectic mixtures of equimolecular proportions of behenic and lignoceric, lignoceric and cerotic acids respectively. The existence of the same acids in the flower wax and in the seed oil is highly interesting.

Experimental

Isolation of the Wax.—Several kilograms of the flowers were obtained from the local market, ground into coarse powder and kept well preserved in stoppered bottles for subsequent work. About 5 k.g. of the powder were extracted with light petroleum ether for about 30 hours in a big Soxhlet extractor in batches of 600 g. The solvent was completely removed by distillation and a green greasy solid mass was finally obtained. It looked like a mixture of chlorophyll and a waxy substance. So it was extracted in the cold with acetone and filtered. Only the chlorophyll went into solution leaving the wax on the filter. This was further extracted several times with acetone until the wax was free from the green chlorophyll. Finally it was crystallised from boiling alcohol and obtained as a colourless solid in an yield of 0·75%. It melted at 73–76°.

In subsequent experiments about 5 k.g. of the powder were extracted just as before using carbon tetrachloride. The removal of chlorophyll and other colouring matter (carotenoids) presented considerable difficulty, most of the solvents dissolving the wax as well as the colouring matter. The purification was only partial with acetone. The method adopted for the final purification of the wax which was coloured was first to dissolve the coloured wax in a little CCl_4, the minimum quantity of solvent being used. Then excess of alcohol was added when the wax was precipitated. This was filtered when the colour passed into the filtrate and the wax was left much lighter in colour. Repetition of this process yielded a pure and almost colourless material melting at 73–76° in an yield of 0·35%.

The wax was sparingly soluble in acetone, chloroform, carbon tetrachloride and cold alcohol. It however dissolved in hot alcohol and when cooled separated in the form of a jelly-like mass which could be filtered under suction. It had the following properties:

Specific Gravity	..	0·98
Saponification Value	..	40·8
Acid Value	..	6·2
Iodine Value	..	1·2
Unsaponifiable Matter	..	70·0%

Unsaponifiable Matter.—The wax was dissolved in a small quantity of benzene and heated with semi-normal alcoholic potash for about 15 hours. The contents were mixed with pumice stone, and the solvents were distilled off and finally they were dried on a water-bath. The dried material was extracted with petroleum ether and acetone successively in a Soxhlet extractor to remove the unsaponifiable matter. The first solvent completely removed the unsaponifiable matter leaving nothing for acetone to extract. This method of extraction was found necessary since the soap formed an emulsion with water and it was found impossible to extract it with petroleum ether or ether.

The unsaponifiable matter consisted of some colourless crystalline material and coloured resinous matter. It was dissolved in excess of hot alcohol and on cooling a colourless crystalline substance was precipitated leaving the filtrate coloured. It was filtered under suction and was found to melt at 80–82°. The chloroform solution of it did not give any colouration with concentrated sulphuric acid and no colouration was produced in Liebermann-Burchard reaction indicating the absence of sterols in it. It was sparingly soluble in acetone, chloroform, ether and cold alcohol. However it readily dissolved in boiling ether and alcohol depositing needle-shaped crystals on cooling. Finally it was recrystallised from ether and it melted at 83–85°. The mixed melting point of this substance with an authentic sample of myricyl alcohol did not exhibit any depression. Finally the whole fraction m.p. 80–82° was boiled with acetic anhydride and anhydrous sodium acetate for 3–4 hours and the contents were thrown into a large excess of water. The precipitated solid was filtered and crystallised from boiling alcohol and ether successively when it was obtained in the shape of fine needles. It melted at 70–71° and did not show any depression in the melting point when mixed with an authentic sample of myricyl acetate. So this fraction was identified as myricyl alcohol. The highly coloured alcohol mother liquor from which myricyl alcohol had been crystallised was treated with bone-char when a yellow solution was obtained. On distilling off the alcohol a small quantity of an yellowish sticky mass melting at 70–80° was obtained. It was dissolved in a small quantity of chloroform and alcohol was added to it till there was slight turbidity and the mixture cooled in the ice-chest. A white solid mixed with traces of yellow resin precipitated out and it was filtered. The precipitate when dissolved in chloroform and a few drops of concentrated H_2SO_4 added, produced orange-red colour in the chloroform layer and the solution exhibited intense green fluorescence. On standing for about half an hour the sulphuric acid layer took up the colour and the chloroform layer became violet. To the chloroform solution of the substance about 20 drops of acetic anhydride were added and the

contents boiled and cooled. Subsequently a drop of concentrated H_2SO_4 was added to it and shaken when slowly a blue solution changing immediately to bluish-green and finally to bright-green was produced. The colour faded to dull-brown in about two hours. When the substance was acetylated as usual with acetic anhydride and anhydrous sodium acetate no crystalline compound could be obtained. However the crude product of acetylation also gave the above colour reactions. The mother liquor from which the above solid was obtained, was distilled off completely when a semisolid coloured mass was left behind. However it gave the usual sterol colour reactions and in Liebermann-Burchard reaction a play of colours was obtained from pink to green.

The Fatty Acids.—After the unsaponifiable matter was extracted, the soap was decomposed in the usual way by boiling with dilute sulphuric acid to liberate the acids. The acids were separated into saturated and unsaturated fractions by Twitchell's[2] lead salt method. The unsaturated acid fraction which was negligible in quantity was rejected and the saturated solid acids were dissolved in boiling alcohol and decolorised by treating the solution with a pinch of animal charcoal. The alcohol solution was slowly concentrated and cooled in the ice-chest when a considerable amount of a colourless solid separated out. On further concentration and subsequent cooling no more solid could be separated from the alcohol solution. The solid was dissolved in a small quantity of ethyl acetate, concentrated and cooled in ice for about four hours when a fraction which softened at 72° was obtained. It was crystallised four times from ethyl acetate and subsequently from alcohol when finally it melted at 76–78°. The molecular weight of this fraction was determined by titrating it with standard potash solution and an average of two experiments gave a value of 380. This may be a mixture of cerotic and lignoceric acids. The ethyl acetate mother liquor did not deposit any more solid on concentration and subsequent cooling. A small amount of 95% alcohol was added to it and cooled in the ice-chest. A solid fraction was obtained which started melting at 69° and finally melted at 74°. This was repeatedly purified by the above process when finally a fraction was obtained which melted at 72–74° and further treatments did not alter the melting point. The molecular weight of this fraction was 350 and probably this may be a mixture of arachidic and lignoceric acids. Finally the mother liquors from which the fraction melting at 72–74° was precipitated and the original alcohol mother liquor were united and the solvent distilled off when a small amount of a solid was obtained. Further fractionation of this solid was tried through different solvents but no definite fraction could be obtained. This melted at 62–64° and its molecular weight (mean of 3 values) was 275. This may be stearic and palmitic acid mixture.

The authors wish to express their gratitude to Prof. T. R. Seshadri for his interest and guidance.

Summary

A colourless wax has been isolated from the flowers of *Butea frondosa* and its physical and chemical properties are described. The unsaponifiable matter consists mainly of myricyl alcohol along with small quantities of steroids. The composition of the saturated fatty acid mixture is very similar to that found in the seed oil.

REFERENCES

1. Katti and Manjunath .. *J. I. C. S.*, 1929, **6**, 839.
   Krishna Rao and Manjunath .. *Ibid.*, 1935, **12**, 611.
2. Twitchell .. *Ind. Eng. Chem.*, 1921, **13**, 806.

OCCURRENCE OF FREE BUTEIN AND BUTIN IN THE FLOWERS OF *BUTEA FRONDOSA*

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Flavanones and chalkones are closely related groups of compounds and are easily interconvertable. For a long time it was thought that in nature chalkones occur exclusively. During the past twenty years methods have been developed for distinguishing readily and definitely between the two classes of compounds. As a result of this, most of the naturally occurring glycosides such as hesperidin, naringin, etc., came to be realised as flavanone derivatives. Chalkones seem to be occurring in nature comparatively infrequently. Carthamine and isocarthamine are claimed to be chalkone glycosides but the evidence does not seem to be quite conclusive. Hence whether butein, one of the fundamental chalkones, occurs free as such in plant products or is obtained only as a result of chemical transformation is a question of great interest.

Hummel and Perkin[1] recorded the isolation of a small quantity of butein from the flowers of *Butea frondosa* and mentioned that it occurs free only in small traces, the major component of the petals being a glucoside of butin. They boiled an aqueous extract of the flowers with sulphuric acid and obtained butin as the main product and butein as the minor product (0·04%). Even this quantity of butein was suspected to be the result of chemical transformation of butin. Lal and Dutt[2] who were the first to isolate butrin, a diglucoside of butin, by careful extraction avoiding acid treatment obtained as a byproduct 0·003% of butein. They treated the alcoholic extract of the flowers with neutral and basic lead acetate solutions in succession, and by the decomposition of the neutral lead salt with hydrogen sulphide isolated butein. In a recent paper Price[3] has studied the yellow pigment present in the Dahlia. He has obtained obviously a very small quantity of butein and seems to be under the impression that his is the first recorded instance of the occurrence of this pigment free in nature. The method adopted by him involves treatment with boiling 0·5% hydrochloric acid for 2 hours and this may not be altogether an indifferent process. In all these cases free butin was not detected.

It has now been found that by using the method of extraction described in the experimental part that butein exists in the free condition in the flower petals of *Butea frondosa* to the extent of about 0·3% and that butin accompanies it in small quantities (0·04%). The treatment employed is so mild that there can be no chemical change which could account for their being formed as secondary products. The important features of the method are (1) the extraction of the aglucones with ether from an aqueous solution of the pigments, (2) their ready solubility in aqueous sodium bicarbonate by means of which they can be extracted from the ether solution and purified and (3) the separation of butin from butein in virtue of the greater solubility of the former in water.

Experimental

3 Kilo-grams of the dried flower powder were extracted repeatedly with petroleum ether or carbon tetrachloride in a large continuous extractor on Soxhlet model in batches of 600 g. for about 30–40 hours. This preliminary treatment removed completely waxy material without extracting any of the yellow colouring matter. Subsequently the powder was rendered free from the last traces of the solvent by blowing air through it and then repeatedly extracted for about 30 hours with 95% alcohol until further extraction gave an almost colourless solution. The alcoholic solution was distilled under reduced pressure to remove the solvent as completely as possible. The residue was treated with a large excess of boiling water (about 2 litres) and allowed to cool. It was found that a clear solution was produced and no resinous solid matter separated out. The solution which was deep orange-yellow in colour was then repeatedly extracted with small quantities of ether till no more colouring matter was extracted and the ether layer was colourless. The collected ether extract was shaken in the cold repeatedly with 1% aqueous sodium bicarbonate. The alkaline aqueous layer rapidly turned red and it could be easily separated from the greenish ether layer. The extraction was continued until the bicarbonate extracted no more colouring matter and remained colourless. A subsequent extraction with aqueous sodium carbonate removed very little colour and hence this extraction was omitted.

The bicarbonate extracts were rendered quickly acid by means of dilute hydrochloric acid so that there might be no possible decompositions. The acid solutions were combined and repeatedly extracted with fresh ether. All the colouring matter was thus extracted and when the ether solution was distilled, it was left behind in a fairly clean condition. It was then dissolved in about 100 c.c. of 95% alcohol and the solution set aside for a week when an orange yellow crystalline solid slowly separated out. This was

recrystallised from dilute alcohol when it was obtained in the form of golden yellow stout needles or rods melting with decomposition at 213–15°. (Found: C, 61·9; H, 4·7; loss on drying at 140°, 6·5%. $C_{15}H_{12}O_5$, H_2O requires C, 62·1; H, 4·8; and loss of H_2O 6·2%.) An alcoholic solution of the substance gave with ferric chloride an olive brown colour and with neutral lead acetate an orange red precipitate. With magnesium and hydrochloric acid it gave rise to no anthocyanin colour indicating the absence of flavanones. The substance was thus identified as butein.

The alcoholic mother liquor from which butein had separated was allowed to concentrate by spontaneous evaporation for one week when a further crop of yellow crystalline solid was obtained. Even after crystallisation from alcohol it melted indefinitely at about 208° and was only pale yellow in colour. It seemed to be a mixture of butein and butin. After all the colouring matter was removed, the alcoholic mother liquor finally contained some slimy resin. The separation of butein and butin was effected by boiling the mixture with about 20 c.c. of water and filtering. The residue on the filter was orange yellow in colour and when crystallised from alcohol was found to be pure butein. The aqueous filtrate slowly deposited a pure yellow crystalline solid (broad rectangular plates). After repeated recrystallisation from small quantities of water it exhibited prominent sintering at about 112° (dehydration) and melted at 224–26°. (Found: C, 59·0; H, 5·4 and loss on drying 12·0%. $C_{15}H_{12}O_5$, $2\,H_2O$ requires C, 58·4; H, 5·2; and loss of H_2O 11·7%.) The anhydrous sample was much lighter in colour. An alcoholic solution gave with ferric chloride a deep green colour and with neutral lead acetate only a dull yellow opalescence. By the addition of a little magnesium powder to the alcohol solution, followed by a few drops of concentrated hydrochloric acid, a brilliant violet colour was developed. This is characteristic of flavanones. From all these properties and reactions it was identified as butin. It may be mentioned here that the dihydrate loses all its water at 100° and there is no further loss on using a higher temperature.

During the course of our experiments it was realised that the mixture of butein and butin could be obtained readily from the ether extract mentioned above by another method. The solution was distilled to remove three-fourths of the solvent and a large excess of petroleum ether added. An orange yellow semi-solid mass readily separated out and turned crystalline on being scratched with a glass rod. Further separation of this mixture was effected as already described.

By the methods adopted above the isolation of the aglucones was quite complete. The ether solution, after the aqueous carbonate extractions,

contained only traces of waxy and amorphous resinous matter. The mixture of free butein and butin was found to be 0·34% on the weight of the air-dry flowers, of which 0·3% was butein and the rest butin.

Summary

A new method of isolating butein and butin from the flowers of *Butea frondosa* is described. The total yield of the aglucones is 0·34% on the weight of the air-dry flowers. By separating them using boiling water, it has been found that butein exists to the extent of 0·3% and butin 0·04%.

REFERENCES

1. Hummel and Perkin .. *J.C.S.*, 1904, 1463.
2. Lal and Dutt .. *J.I.C.S.*, 1935, 262.
3. Price . *J.C.S.*, 1939, 1017.

SCATTERING OF POLARISED LIGHT IN COLLOIDS

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1. Introduction

When an unpolarised beam of light is passed through a colloidal medium, the light scattered in the transverse horizontal direction is found to be partially polarised. If we consider the incident light as made up of two beams of equal intensity and unrelated in phase, one with vibrations vertical and the other horizontal, the light scattered transversely will consist of vertically polarised parts, V_v and V_h arising out of these two beams respectively, and horizontally polarised parts H_v and H_h also due to them. The depolarisation factors, ρ_u when the incident light is unpolarised, ρ_v when it is vertically polarised and ρ_h when it is horizontally polarised are given by

$$\rho_u = \frac{H_v + H_h}{V_v + V_h}, \quad \rho_v = \frac{H_v}{V_v} \text{ and } \rho_h = \frac{V_h}{H_h}.$$

Arguing from the fact that the components H_v and V_h are related to each other in a reciprocal fashion and should therefore be of equal intensity, Krishnan (1935) has deduced the following relation connecting ρ_u, ρ_v and ρ_h:

$$\rho_u = (1 + 1/\rho_h)/(1 + 1/\rho_v).$$

It has been demonstrated experimentally by Krishnan (1935), Subbaramiah (1937) and Geham and Field (1937) that this relation is valid for all wavelengths and for colloidal particles of any size, shape and structure provided they are arbitrarily orientated in space.

In a recent paper Krishnan (1939) has attempted to develop the above considerations to the case of the incident light polarised in any azimuth. If θ is the angle made by the plane of polarisation of the incident beam with the vertical, it may be resolved into components with intensity proportional to $\cos^2\theta$ along the vertical and $\sin^2\theta$ along the horizontal. In the transversely scattered light, the vertical part gives rise to two components, $V_v \cos^2\theta$ and $H_v \cos^2\theta$, and the horizontal part gives rise to two others, $V_h \sin^2\theta$ and $H_h \sin^2\theta$, along the vertical and horizontal directions respectively.

If it could be assumed that the components of the scattered light whose vibration directions are coincident, are uncorrelated in phase in spite of the fact that the components in the incident light which give rise to them are in exact phase-relationship, the depolarisation factor for the azimuth θ could be written as:

$$\rho_\theta = \frac{\text{The sum of horizontal components}}{\text{The sum of vertical components}}$$

$$= \frac{H_h \sin^2\theta + H_v \cos^2\theta}{V_h \sin^2\theta + V_v \cos^2\theta} = \frac{1 + \tan^2\theta/\rho_h}{\tan^2\theta + \dfrac{1}{\rho_v}}$$

since $H_v = V_h$. Krishnan's preliminary measurements for graphite sol, arsenious sulphide sol and toluene emulsions showed that there is a rough agreement between the observed value of ρ_θ and that calculated from ρ_v and ρ_h using the above formula. The deviation, nevertheless, becomes significant in the case of large anisotropic particles. In the present communication the author has made an extended study of the problem with a view to ascertain under what conditions the proposed formula fails.

2. *Experimental arrangements and results*

The experimental set-up is schematically illustrated in Fig. 1. Light from a carbon arc working at a current of 15 amps. was focussed by means

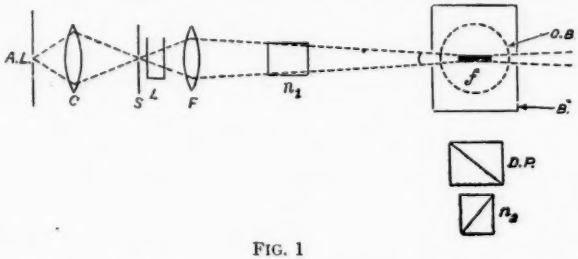

FIG. 1

of a large condensing lens C on a narrow aperture ($1 \cdot 5 \times 2$ mm.) S. The emerging beam of light is passed through a rectangular cell containing alum solution and was brought to a focus f by a lens F of low aperture ratio. The observation bulb (O.B.) containing the liquid is enclosed in a wooden box B. lined inside with black velvet and with holes for the ingress and egress of light and placed at the focus f. A polarising nicol n_1 mounted on a circular scale is placed between the wooden box and the lens F and by rotating the nicol, the incident beam is polarised with the plane of vibration making any known angle with the vertical. The scattered light is first split into the horizontal and vertical components by a double-image prism D.P.,

TABLE I

Graphite sol centrifuged for different intervals

ϑ°	Centrifuged for 5 min.		Centrifuged for 15 min.		Centrifuged for 30 min.		Centrifuged for 45 min.	
	ρ_θ Obs.	ρ_θ Calc.	ρ_θ Obs.	ρ_θ Calc.	ρ_θ Obs.	ρ_θ Calc.	ρ_θ Obs.	ρ_θ Calc.
0 (ρ_v)	·060	..	·060	..	·060	..	·058	..
10	·061	·069	·062	·069	·062	·068	·061	·068
20	·086	·096	·068	·095	·078	·094	·086	·086
30	·107	·151	·107	·153	·121	·143	·116	·129
40	·217	·247	·174	·245	·180	·231	·191	·201
50	·358	·421	·287	·419	·343	·390	·328	·344
60	·635	·746	·506	·742	·697	·739	·570	·610
70	1·147	1·493	·990	1·489	1·096	1·369	1·131	1·192
80	2·657	3·084	2·270	3·060	2·541	2·811	2·410	2·480
90	4·651	..	4·620	..	4·220	..	3·771	..

TABLE II

θ°	Vanadium pentoxide sol		Iron oxide sol		As_2S_3 sol		Sulphur sol	
	ρ_θ Obs.	ρ_θ Calc.	ρ_θ Obs.	ρ_θ Calc.	ρ_θ Obs.	ρ_θ Calc.	ρ_θ Obs.	ρ_θ Calc.
0 (ρ_v)	·050	..	·005	..	·027	..	·004	..
10	·054	·054	·007	·006	·039	·039	·016	·011
20	·064	·065	·009	·009	·068	·076	·056	·034
30	·077	·090	·017	·014	·137	·148	·123	·079
40	·103	·133	·027	·023	·247	·280	·226	·162
50	·147	·211	·040	·041	·476	·528	·450	·323
60	·299	·365	·080	·079	1·038	1·042	·862	·693
70	·632	·713	·159	·186	2·348	2·32	1·676	1·66
80	1·497	1·532	·406	·643	6·655	6·296	6·503	6·457
90	2·441	..	4·544	..	13·44	..	15·02	..

TABLE III

θ	Benzene		Acetic acid	
	ρ_θ Obs.	ρ_θ Calc.	ρ_θ Obs.	ρ_θ Calc.
0 (ρ_v)	·253	..	·257	..
10	·282	·278	·270	·263
20	·296	·282	·301	·282
30	·341	·313	·335	·316
40	·405	·372	·414	·371
50	·527	·460	·468	·456
60	·651	·593	·638	·581
70	·844	·756	·704	·750
80	1·000	·950	·932	·920
90	1·000	..	1·000	..

and the ratio of the intensities of these components is determined by the usual method making use of an analysing nicol n_2. Observations are repeated several times for each azimuthal angle and the average is taken. Tables I, II and III give the observed and calculated values of depolarisation ρ_θ for angles varying from 0° to 90°, for benzene, acetic acid, arsenious sulphide, sulphur, vanadium pentoxide and iron oxide sols, and graphite sols centrifuged for different intervals of time at a speed of 3000 R. P. M. In the tables $\rho_{90°}$ is evidently $1/\rho_h$ as defined above.

3. *Discussion*

As Krishnan has shown in his paper, it should be theoretically expected that the experimentally observed value of ρ_θ should agree with that calculated from ρ_v and ρ_h both in the case of media consisting of very small, anisotropic particles such as in pure liquids and also for colloids containing spherical isotropic particles of any size. These values for benzene and acetic acid are given in Table III and show that, within experimental error, this expectation is justified. It should be pointed out that the calculated value is generally lower than the observed and the deviation has a maximum value of 10% which should be taken as the maximum probable experimental error in this investigation. The scattering of light by the pure liquids is, however, very feeble and the observational error involved would be considerably greater

than that in scattering by colloids. Among the colloids studied, arsenious sulphide sol shows good agreement between the observed and calculated values of ρ_θ. In all the other cases the deviation is more or less pronounced. For graphite, vanadium pentoxide and iron oxide sols, the calculated value is, in general, greater than that observed. This deviation is in the opposite direction for sulphur sol.

The dependence of the deviation on the particle size and distribution is well brought out in Table I in which the data for graphite sol after four different stages of centrifuging are given. This sol contains large ellipsoidal particles. As the centrifuging progresses, the particles become smaller and more uniform. Corresponding to this change in the size of the particles, there is also an observable diminution in the deviation. While the sol after 5 and 15 minutes centrifuging gives a difference as high as 40%, that after 45 minutes centrifuging shows very little deviation.

The observed deviation may probably be due to the following causes: When the sol is no longer dilute, secondary scattering becomes prominent and the depolarisation factor is considerably influenced by its state of polarisation. We may state that, in general, this would tend to make the calculated value lower than the observed. The deviation due to this cause alone is illustrated by the sulphur sol, which as shown by the very low value of ρ_v and the large value of $\rho_{90°}$ consists of large spherical particles. The second cause of deviation arises in the case of large anisotropic particles in which *the assumption that the components of scattering which have the same direction of vibration are incoherent is evidently no longer valid.* It is significant to note that the result of a partial coherence between the components is to diminish the value of ρ_θ, as may be seen from the fact that for the graphite and vanadium pentoxide sols the calculated values are consistently higher than that observed. As the particles become smaller in size, as for example, the graphite sol on centrifuging for longer intervals of time, the assumption of incoherence is more nearly valid as is shown by the deviation becoming less.

The author wishes to express his heart-felt thanks to Sir C. V. Raman for suggesting the problem and for his continued interest in the work, and his indebtedness to Dr. C. S. Venkateswaran for useful advice and assistance.

4. *Summary*

The depolarisation of transversely scattered light by colloids having different particle size and shape is investigated with incident light polarised in any azimuth. The results are compared with the depolarisation factor calculated from an expression connecting ρ_v, ρ_h and ρ_θ, where θ is the azimuthal

angle. The divergence between the calculated and observed values is small for benzene and acetic acid, and arsenious sulphide sol but becomes greater with increasing particle size and anisotropy. This is clearly demonstrated by graphite sols centrifuged for various intervals of time. The observed deviation is explained as due partly to the influence of secondary scattering and partly to the assumption of incoherence between the different types of scattering not being strictly valid for large anisotropic particles.

REFERENCES

1. Krishnan, R. S. .. *Proc. Ind. Acad. Sci.*, (A), 1935, **1**, 782, 915; **2**, 221.
2. Subbaramiah, K. .. *Ibid.*, 1937, **5**, 128 and 138.
3. Geham, S. D., and Field, J. E. .. *Ind. Eng. Chem.*, 1937, **29**, 793.
4. Krishnan, R. S. .. *Proc. Ind. Acad. Sci.* (A), 1939, **10**, 395.

TRANSVERSE VIBRATIONS OF TRIANGULAR MEMBRANES

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The solutions for the transverse vibrations of circular and rectangular membranes are well known. The case of a right-angled isosceles triangular membrane can be as easily solved as that of a rectangular one,[1] and that of an equilateral triangular membrane has been discussed by Lamé who finds that the frequency, $(p/2\pi)$, is given by

$$\frac{p}{2\pi} = \frac{c}{a}(m^2 + n^2 + mn)^{\frac{1}{2}}, \quad [m, n \text{ integers}] \tag{1}$$

a being the height of the triangle and c the ratio of the uniform tension T_1 and the superficial density ρ. If z be the displacement, Routh[2] has given in terms of trilinear co-ordinates the particular solution obtained from (1) by putting m or $n = 0$ as

$$z = \sin \frac{n\pi\alpha}{a} \sin \frac{n\pi\beta}{a} \sin \frac{n\pi\gamma}{a} \cos pt, \tag{2}$$

α, β, γ being the trilinear co-ordinates. This particular solution has also been recently obtained by D. G. Christopherson.[3]

As Lamé's Leçons Sur L' Elasticite in which the general solution (1) is given is not readily available, it has been independently obtained in this paper. New results have been obtained for:

(*a*) an isosceles triangle containing an angle of 120°;

(*b*) a right-angled triangle containing an angle of 60°.

If x, y, z are the co-ordinates of a point of the membrane in the displaced position, the xy plane coinciding with the equilibrium position, we know that for small displacements z should satisfy

$$\frac{\partial^2 z}{\partial t^2} = c^2\left(\frac{\partial^2 z}{\partial x^2} + \frac{\partial^2 z}{\partial y^2}\right). \tag{3}$$

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[1] Rayleigh, *Theory of Sound*, I, 1894, pp. 317–18.

[2] Routh, *Advanced Rigid Dynamics*, 1905, p. 457.

[3] D. G. Christopherson, *Quart. J. of Math.*, 1940, **11**, p. 65.

If we assume the time factor in z to be of the form A cos $(pt + \epsilon)$, (3) becomes

$$\frac{\partial^2 z}{\partial x^2} + \frac{\partial^2 z}{\partial y^2} + \frac{p^2}{c^2} z = 0. \tag{3·1}$$

The solution of (3·1) may be written in the form

$$z = \begin{matrix}\sin \\ \cos\end{matrix}\left(\frac{p \cos \theta}{c} x\right) \begin{matrix}\sin \\ \cos\end{matrix}\left(\frac{p \sin \theta}{c} y\right). \tag{4}$$

Isosceles Triangular Membranes

Let the vertical angle of the triangle be 2α. Let us take the origin at the vertex and the axes of x and y perpendicular and parallel to the base of the triangle. The sides of the triangle are $x = a$, $y = \pm x \tan \alpha$. One form of z satisfying the boundary condition $z = 0$ is

$$z = \cos \frac{(2m+1)\pi x}{2a} \cos \frac{(2n+1)\pi y}{2a \tan \alpha} - \cos \frac{(2n+1)\pi x}{2a} \cos \frac{(2m+1)\pi y}{2a \tan \alpha}, \tag{5}$$

m and n being integers. This satisfies (3) only when $\alpha = \frac{1}{4}\pi$, and then we have

$$p^2 = \frac{c^2 \pi^2}{4a^2} \{(2m+1)^2 + (2n+1)^2\}, \tag{6}$$

the gravest mode being given by $m = 0, n = 1$, that is,

$$\frac{p}{2\pi} = \frac{c}{2a} \sqrt{2 \cdot 5} = (0 \cdot 791) \frac{c}{a}. \tag{7}$$

This solution gives the asymmetrical vibrations of a right-angled isosceles membrane. The symmetrical are given by

$$z = \sin \frac{m\pi x}{a} \sin \frac{n\pi y}{a} - \sin \frac{n\pi x}{a} \sin \frac{m\pi y}{a}, \tag{8}$$

which obviously makes $y = 0$ a nodal line.

Equilateral membrane.—If we put

$$z = 2 \sin \frac{(m-n)\pi x}{a} \cos \frac{(m+n)\pi y}{a \tan \alpha}$$

$$- 2 \sin \frac{(2m+n)\pi x}{a} \cos \frac{n\pi y}{a \tan \alpha} + 2 \sin \frac{(2n+m)\pi x}{a} \cos \frac{m\pi y}{a \tan \alpha}, \tag{9}$$

m, n being integers, we see that the boundary condition is satisfied for any isosceles triangle. But it exactly satisfies (3) only when $\alpha = \frac{1}{6}\pi$, and in that case[4]

$$\frac{p}{2\pi} = \frac{c}{a} (m^2 + n^2 + mn)^{\frac{1}{2}}. \tag{10}$$

[4]This solution also holds good for the symmetrical vibrations of a rhombus of angle 120° with the shorter diagonal as a nodal line.

This gives the asymmetrical vibrations of an equilateral membrane. The gravest mode is given by

$$z = 2 \sin \frac{2\pi x}{a} - 4 \sin \frac{\pi x}{a} \cos \frac{\pi y \sqrt{3}}{a}, \tag{11·1}$$

$$\frac{p}{2\pi} = \frac{c}{a}. \tag{11·2}$$

If we put $n = 0$ in (9), we get the result to which (2) reduces when changed into Cartesian co-ordinates, and which has been also obtained by Christopherson.

The symmetrical modes are given by

$$\begin{aligned} z = {} & 2 \sin \frac{(m-n)\pi x}{a} \sin \frac{(m+n)\pi y \sqrt{3}}{a} \\ & + 2 \sin \frac{(2m+n)\pi x}{a} \sin \frac{n\pi y \sqrt{3}}{a} \\ & - 2 \sin \frac{(2n+m)\pi x}{a} \sin \frac{m\pi y \sqrt{3}}{a}. \end{aligned} \tag{12}$$

All the three medians are now nodal lines.

Isosceles Triangle Containing an Angle of 120°

In this case we put

$$\begin{aligned} z = {} & 2 \sin \frac{(m-n)\pi x}{a} \sin \frac{(m+n+1)\pi y \tan \alpha}{a} \\ & - 2 \cos \left(2m + 1 + \frac{2n+1}{2}\right) \frac{\pi x}{a} \cos \frac{(2n+1)\pi y \tan a}{2a} \\ & + 2 \cos \left(2n + 1 + \frac{2m+1}{2}\right) \frac{\pi x}{a} \cos \frac{(2m+1)\pi y \tan \alpha}{2a}. \end{aligned} \tag{13}$$

This makes $z = 0$ on the boundary and satisfies (3) if $\alpha = \frac{1}{3}\pi$ and the sides are given by $x = a$, $y = x\sqrt{3}$, $y + x\sqrt{3} = 2a/\sqrt{3}$. The general expression for the frequency is now given by

$$\frac{p}{2\pi} = \tfrac{1}{2} \frac{c}{a} \{(2m+1)^2 + (2n+1)^2 + (2m+1)(2n+1)\}^{\frac{1}{2}}. \tag{14}$$

In the gravest mode we have

$$\begin{aligned} z = {} & 2 \sin \frac{2\pi x}{a} \sin \frac{\pi y \sqrt{3}}{a} - 2 \cos \frac{5\pi x}{2a} \cos \frac{\pi y \sqrt{3}}{2a} \\ & + 2 \cos \frac{\pi x}{2a} \cos \frac{3\pi y \sqrt{3}}{2a}, \end{aligned} \tag{15·1}$$

$$\frac{p}{2\pi} = \tfrac{1}{2}\sqrt{7} \frac{c}{a} = (1{\cdot}323) \frac{c}{a} = (0{\cdot}882) \frac{c}{h}. \tag{15·2}$$

These give the symmetrical vibrations of an isosceles triangular membrane of height h containing an angle of 120°. $y = a/\sqrt{3}$ is a nodal line and the gravest mode appears to be symmetrical.

Right-angled Triangle Containing an Angle of 60°

In this case we can take the sides as $y = a/\sqrt{3}$, $x = a$, $y = x\sqrt{3}$. The result for this case follows at once from the symmetrical vibrations of an isosceles triangle containing an angle of 120°. We easily see that z is of the same form as given in (13). The lowest tone is given by (15). The general form of the frequency is the same as given in (14).

It has not been found possible to get an exact solution for any other case excepting the four discussed above. In all other cases an approximate value of the gravest mode may be obtained by using Rayleigh's method when the normal types cannnot be accurately determined.

NEW BANDS IN THE TRIPLET CARBON SYSTEM

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The triplet carbon bands were discovered by Merton and Johnson[1] in the spectrum of an uncondensed discharge through a tube with carbon electrodes and containing helium at a pressure of about 20 mm. of Hg. Birge[2] gave the vibrational quantum analysis of the bands and suggested that their final electronic state is very probably identical with that of the third positive bands of carbon. Following the discovery of Cameron bands[3] and their analysis and interpretation by Johnson[4], the third positive carbon bands and consequently the triplet carbon bands, could be definitely attributed to CO. These bands are more easily developed in the presence of a rare gas than in its absence and not only helium[1] but argon[5] and neon[6] also favour their production.

Recently, L. Gerö with F. Szabo[6] has done the rotational analysis of some of these bands and shows that they are due to the transition $d^3\Pi_{\text{inv.}} \rightarrow a^3\Pi_{\text{reg.}}$, the latter being also the final level of the third positive bands of CO. Assuming the band at $\nu = 15540$ cm.$^{-1}$ to be the (O, O) band, the following equation is deduced to represent the null lines of the bands of $v'' = 0$ progression:

$$\nu = 14987{\cdot}66 + 1105{\cdot}82\, u' - 8{\cdot}272\, u'^2 - 0{\cdot}1125\, u'^3 \qquad (1)$$

where, $u' = (v' + \frac{1}{2})$. The position of the $d^3\Pi_1$ level relative to the ground level is also calculated as $\nu = 64013{\cdot}3$ cm.$^{-1}$, the origin of the system being observed at $\nu = 15538{\cdot}5$ cm.$^{-1}$

A further study of the bands shows, however, that the band at $\nu =$ 15540 cm.$^{-1}$ is not the (O, O) band of the system. Three new bands on the higher wave-length side have been photographed on suitable far-red sensitive plates from the spectrum of a discharge tube showing the triplet system as developed in the presence of helium. The resolving instrument used was a Littrow type Hilger E_1 glass spectrograph having an average dispersion of 31 A/mm. between $\lambda\lambda$ 6850 and 7550 A.U. These new bands fit into the existing v', v'' table but necessitate an increase of two units in the present v' quantum numbers. The wave-numbers of the band heads *in vacuo*, probably accurate to $\pm$ 3 cm.$^{-1}$ are displayed in the following

table which shows their connection to the band at 15540 cm.$^{-1}$ and forms therefore, the extension of the existing table.

v'' / v'_e	O		1
	13326		
	303 †		
0	346		
	374		
	387		
dif.	*1129, 1133, 1125, 1129, 1129*		
	14355		
	436		
1	471		
	503		
	516		
dif.	*1110, 1104, 1108, 1108, 1107*		
	(15465)	*dif.*	..
	(15540)	*1715*	13825
2	15579	*1712*	867
	(15661)	*1710*	901*
	(15623)	*1712*	911

† Indicates a probable perturbation.

* Confused with other bands.

(1) The new bands here reported are those *not* included in brackets.

(2) Incidentally, it may be mentioned that four heads have been recorded by Merton and Johnson for most of the bands of this system but an additional head for some of them is clearly shown on the present plates. This extra head, third in the above table in each of the bands is probably due to the branch designated by Gerö as $^{S}R_{33}$.

It should be mentioned that it is not certain whether the band at $\nu = 13303$ cm.$^{-1}$ is definitely the (O, O) band as shown here. It is likely that the origin may be higher up in the near infra-red region beyond the range of the present investigation. Assuming, however, that the one shown

here is the (O, O) band and that there are no perturbations, equation (1) transforms, on extrapolation, to,

$$\nu = 12743{\cdot}8 + 1137{\cdot}79\,u' - 7{\cdot}624\,u'^2 - 0{\cdot}1125\,u'^3.$$

Hence also the position of the $d^3\Pi_1$ level from the ground level of the CO molecule is calculated as 61785·5 cm.$^{-1}$, the origin of the system, on extrapolation, being at $\nu = 13310{\cdot}7$ *cm.*$^{-1}$

Summary

A few new band heads belonging to the triplet carbon band system of CO are reported. These necessitate an increase of two units in the existing v' numbering. The origin of the system may be still further in the region of longer waves but is definitely shifted at least to $\nu = 13310{\cdot}7$ cm.$^{-1}$ according to these new results, thus locating the $d^3\Pi_1$ level at 61785·5 cm.$^{-1}$ from the ground level of the CO molecule.

REFERENCES

1. T. R. Merton and R. C. Johnson .. *Proc. Roy. Soc.* (A), 1923, **103**, 383.
2. R. T. Birge .. .. *Nature*, 1925, **116**, 171.
3. W. H. B. Cameron .. .. *Phil. Mag.*, 1926, **1**, 405.
4. R. C. Johnson .. .. *Nature*, 1926, **117**, 376.
5. ———— .. .. *Proc. Roy. Soc.* (*A*), 1924, **106**, 195.
6. L. Gerö with F. Szabo .. .. *Ann. der. Phys.*, 1939, **35·7**, 597.

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